Results and Discussions

RESULTS and DISCUSSIONS

1. Sample Preparation:

Wood pulp samples were treated with sodium hydroxide of different concentrations 2, 6, 10, 14, 18 % in presence of 0.5 % zinc chloride at 100 ^{o}C and 1:15 liquor ratio for 1 hour. The samples were washed with distilled water till free of alkali. The samples were treated with 10 % acetic acid, washed with distilled water till neutrality, and dried at room temperature. Paper samples were then prepared from samples treated with different sodium hydroxide concentrations and were compared with untreated samples (blank sample). Each sample was then divided to five portions, one left as it and the other portions were then heated at 100 ^{o}C for different time intervals 24, 48, 72 and 96 hours. Different conditions for samples treatment are given in table (1).

Table 1: **Different conditions for samples treatment**

NO.	Sample	Heat treatment	Time of Heat treatment
1	Original	---	---
2	Original	100°C	24 hrs
3	Original	100°C	48 hrs
4	Original	100°C	72 hrs
5	Original	100°C	96 hrs
6	2% NaOH +0.5% $ZnCl_2$	---	---
7	2% NaOH +0.5% $ZnCl_2$	100°C	24 hrs
8	2% NaOH +0.5% $ZnCl_2$	100°C	48 hrs
9	2% NaOH +0.5% $ZnCl_2$	100°C	72 hrs
10	2% NaOH +0.5% $ZnCl_2$	100°C	96 hrs
11	6% NaOH +0.5% $ZnCl_2$	---	---
12	6% NaOH +0.5% $ZnCl_2$	100°C	24 hrs
13	6% NaOH +0.5% $ZnCl_2$	100°C	48 hrs
14	6% NaOH +0.5% $ZnCl_2$	100°C	72 hrs
15	6% NaOH +0.5% $ZnCl_2$	100°C	96 hrs
16	10% NaOH +0.5% $ZnCl_2$	---	---
17	10% NaOH +0.5% $ZnCl_2$	100°C	24 hrs
18	10% NaOH +0.5% $ZnCl_2$	100°C	48 hrs
19	10% NaOH +0.5% $ZnCl_2$	100°C	72 hrs
20	10% NaOH +0.5% $ZnCl_2$	100°C	96 hrs
21	14% NaOH +0.5% $ZnCl_2$	---	---
22	14% NaOH +0.5% $ZnCl_2$	100°C	24 hrs
23	14% NaOH +0.5% $ZnCl_2$	100°C	48 hrs
24	14% NaOH +0.5% $ZnCl_2$	100°C	72 hrs
25	14% NaOH +0.5% $ZnCl_2$	100°C	96 hrs
26	18% NaOH +0.5% $ZnCl_2$	---	---
27	18% NaOH +0.5% $ZnCl_2$	100°C	24 hrs
28	18% NaOH +0.5% $ZnCl_2$	100°C	48 hrs
29	18% NaOH +0.5% $ZnCl_2$	100°C	72 hrs
30	18% NaOH +0.5% $ZnCl_2$	100°C	96 hrs

2. Effect of heat treatment (aging) on the physical properties of paper sheets (Blank sample):

The effect of artificial aging on the untreated samples was extensively studied. The data are cited in table (2) and are shown graphically in fig. (1). Inspection of the data given shows that:

- The elongation percent decreases by increasing the time intervals of heat treatment (thermal aging), where it decreases from o.290% to 0.244 %. The former value represents elongation percent for the thermally untreated sample while the latter represents 96 hours of thermal treatment. Thus, about 16 % decrease in elongation took place upon heat treatment at 100 ^{o}C for 96 hours.
- The effect of thermal treatment on the breaking length showed the same trend, where it decrease form 6908 m for the untreated sample to 5550 m for sample number 5 (thermally treated at 100 ^{o}C for 96 hours). So, about 13 % decrease in breaking length was obtained by 96 hours heat treatment at 100 ^{o}C.
- Similar behavior was obtained for the burst factor, where a 13.5% decrease was obtained by thermal treatment at 100 ^{o}C for 96 hours.
- As gained from X-ray, crystallinity increased as a result of aging from 54.6 to 65.8, this indicates that heat treatment makes the cellulose chains more ordered.
- Also the degree of polymerization increased from 913 to 1179 as a result of heat treatment for the blank samples.

In brief we can say that the heat treatment at 100 ^{o}C for time intervals up to 96 hours resulted in decreasing the Elongation percent, Breaking length and Burst factor, while X-ray showed that crystallinity and degree of polymerization increased.

Table 2: Physical properties of Blank sample without alkali treatment

NO	Thermal Treatment	Elongation %	Breaking Length (m)	Burst Factor	X-Ray Crystallinity	Degree of Polymerization
1	without	0.290	6908	51.28	54.6	914
2	24 hrs	0.267	6602	48.62	60.4	986
3	48 hrs	0.259	6260	47.71	62.6	1035
4	72 hrs	0.249	6090	44.84	64	1106
5	96 hrs	0.244	5550	44.39	65.8	1179

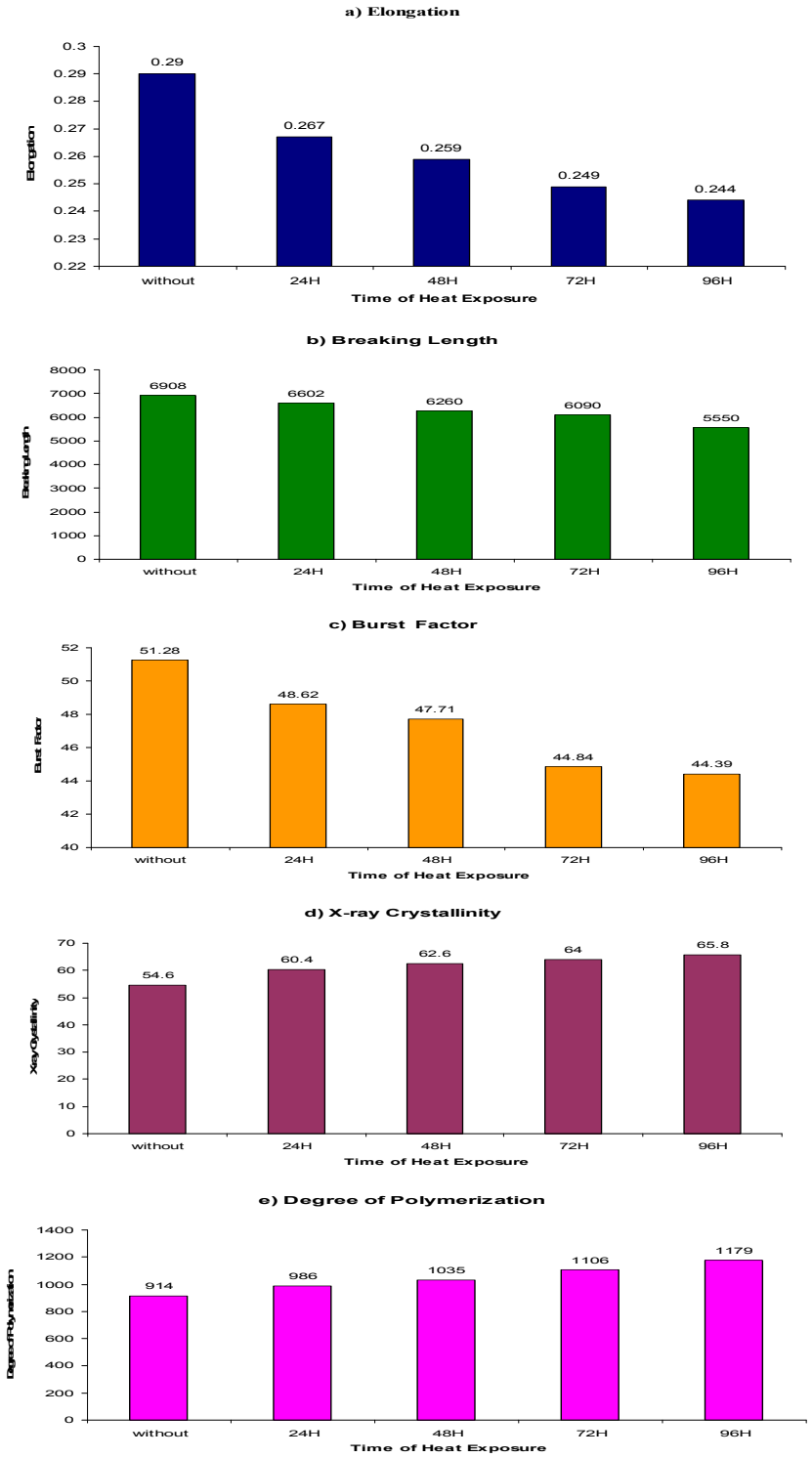


Fig. 1: Physical properties of Blank sample without chemical treatment

3. Effect of treatment with sodium hydroxide solutions on the physical properties of paper sheets:

3.1. Thermally treated samples:

The effect of sodium hydroxide solutions of increasing concentrations (2 %, 6 %, 10 %, 14 % and 18 %) on the physical properties of the thermal untreated samples (6, 11, 16, 21 and 26) was studied and compared to those of the blank sample (sample 1). The data are represented numerically in table (3) and shown graphically in fig. (2). From the results obtained, it was found that:

- Elongation percent decreased by increasing the concentration of sodium hydroxide (from 2 % to 18 %). The blank sample (without sodium hydroxide treatment) gives an elongation of 0.29 %. The samples treated with 2% sodium hydroxide; the elongation is only 0.246 % and so on until it reaches 0.198 % for the sample treated with 18 % sodium hydroxide. The decrease in elongation percent reaches 22 % at 18 % sodium hydroxide treatment.
- The effect of sodium hydroxide treatment on breaking length of paper sheets showed slightly different behaviour. Firstly an increase in the breaking length was obtained from the blank sample; 6908 m to 7397 m in case of treatment with 2 % sodium hydroxide solution (sample 6). On increasing the concentration of sodium hydroxide from 2 % to 18 %, the breaking length exhibited a total decrease of 70 %. The first increase taking place from the untreated sample to that of the treated with 2 % sodium hydroxide is due to the slight refining of the 2% sodium hydroxide treatment where it removed the very sheet cellulose chains only.

- The burst factor is the most affected property due to the sodium hydroxide treatment where a loss of about 84 % took place due to 18% sodium hydroxide treatment. The blank sample gave a value of 51.28 whereas the treated sample with 18 % sodium hydroxide gave only 7.99.
- X-ray determined crystallinity is moderately affected and it lost 25 % of its initial value due to the sodium hydroxide treatment (c.f. table 3).
- The degree of polymerization is also moderately affected by increasing sodium hydroxide concentrations. A decrease by about 45 % from the original value (blank sample) was obtained after treatment with 18 % sodium hydroxide solution at the same temperature (c.f. table 3), whereas that which treated with 18 % sodium hydroxide gives only 572.

Table 3: Physical properties of samples treated with sodium hydroxide

NO.	Conc. of NaOH	Elongation m	Breaking Length %	Burst Factor	X –Ray Crystallinity	Degree of Polymerization.
1	without	0.29	6908	51.28	54.6	914
6	2%	0.246	7397	43.5	53	876
11	6%	0.231	5294	33.1	50	788
16	10%	0.22	3954	21.75	48	676
21	14%	0.207	2870	14.05	45.7	594
26	18%	0.198	2076	7.99	43.1	572

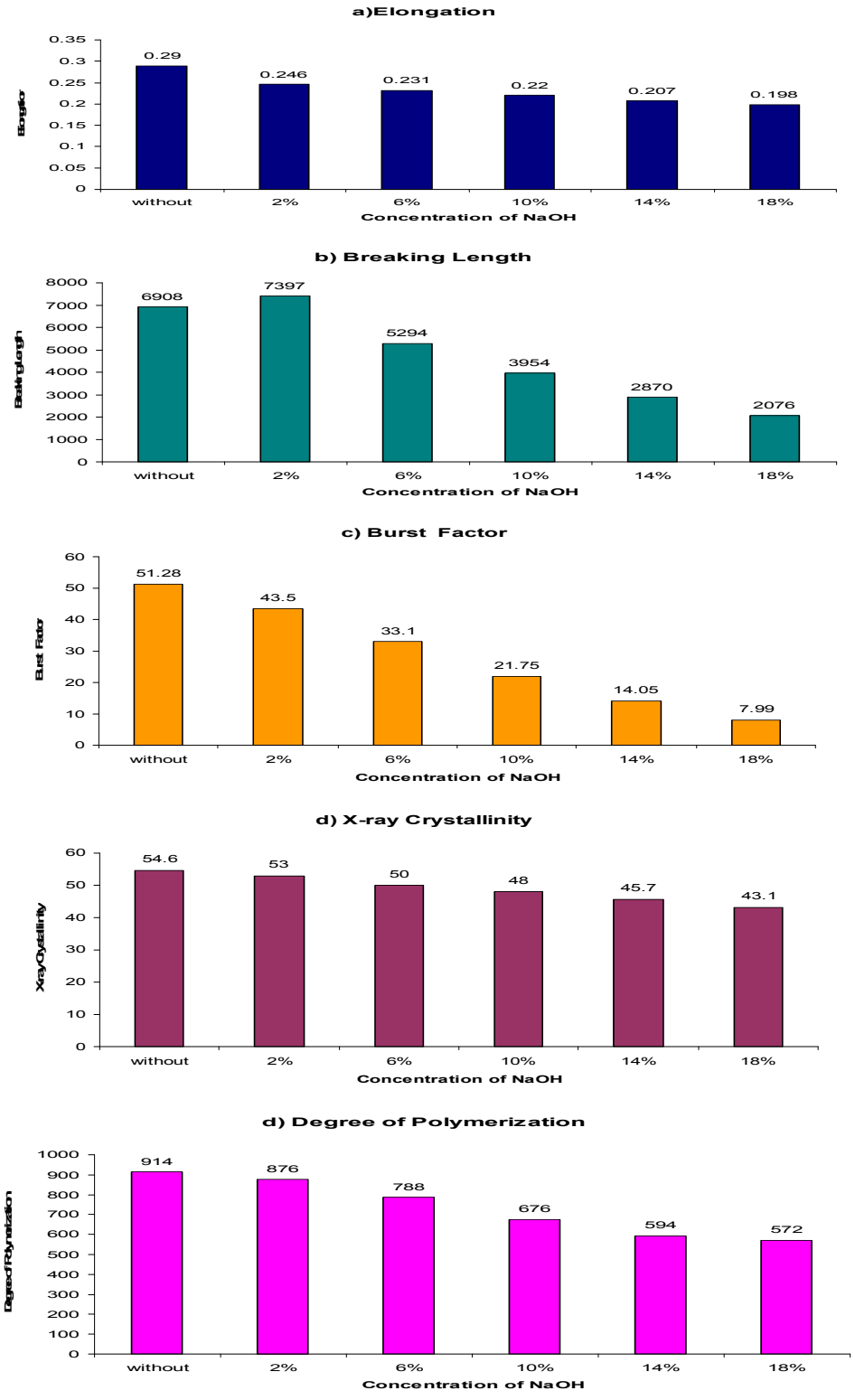


Fig. 2: Physical properties of the samples treated with sodium hydroxide

3.2. Effect of treatment with 2 % sodium hydroxide and 0.5 % zinc chloride at different time intervals on the physical properties of paper sheets:

The effect of treatment with 2 % sodium hydroxide and 0.5 % zinc chloride (at different time intervals) on the physical properties of the thermally treated paper sheets was extensively studied. The data are represented in table (4) and in fig. (3). From the results obtained, it was found that:

- The elongation percent decreased from 0.246 % to 0.207%, that is to say a decrease of about 16 % took place due to the heat treatment (aging) at 100 ^{o}C for 96 hours.
- Considering the breaking length, it also decreased from 7397 m. to 6012 m., i.e. a decrease of about 19 % resulted due to the heat treatment; this can be attributed to the oxidation of the cellulose chains taking place during aging.
- Burst factor also decreased from 43.5 to 38.85 as a result of aging for 96 hours. So a decrease of about 11 % takes place. The decrease of the above mentioned properties are attributed to the oxidation of cellulose during aging times.
- For X-ray determined crystallinity, it increased after 24 hours then decreased after that till reach the original value after 96 hours.
- The same trend was noticed for the degree of polymerization i.e. an increase was noticed after 24 hours then a decrease can be noticed for times more than 24 hours.

Table 4: Physical properties of the samples treated with 2 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

NO.	Thermal Treatment	Elongation %	Breaking Length m.	Burst Factor	X –Ray Crystallinity	Degree of Polymerization
6	without	0.246	7397	43.5	53	876
7	24 hrs	0.230	7039	42.28	57.3	1114
8	48 hrs	0.224	6569	41,92	56.3	936
9	72 hrs	0.210	6412	39.04	54.8	862
10	96 hrs	0.207	6012	38.85	54	817

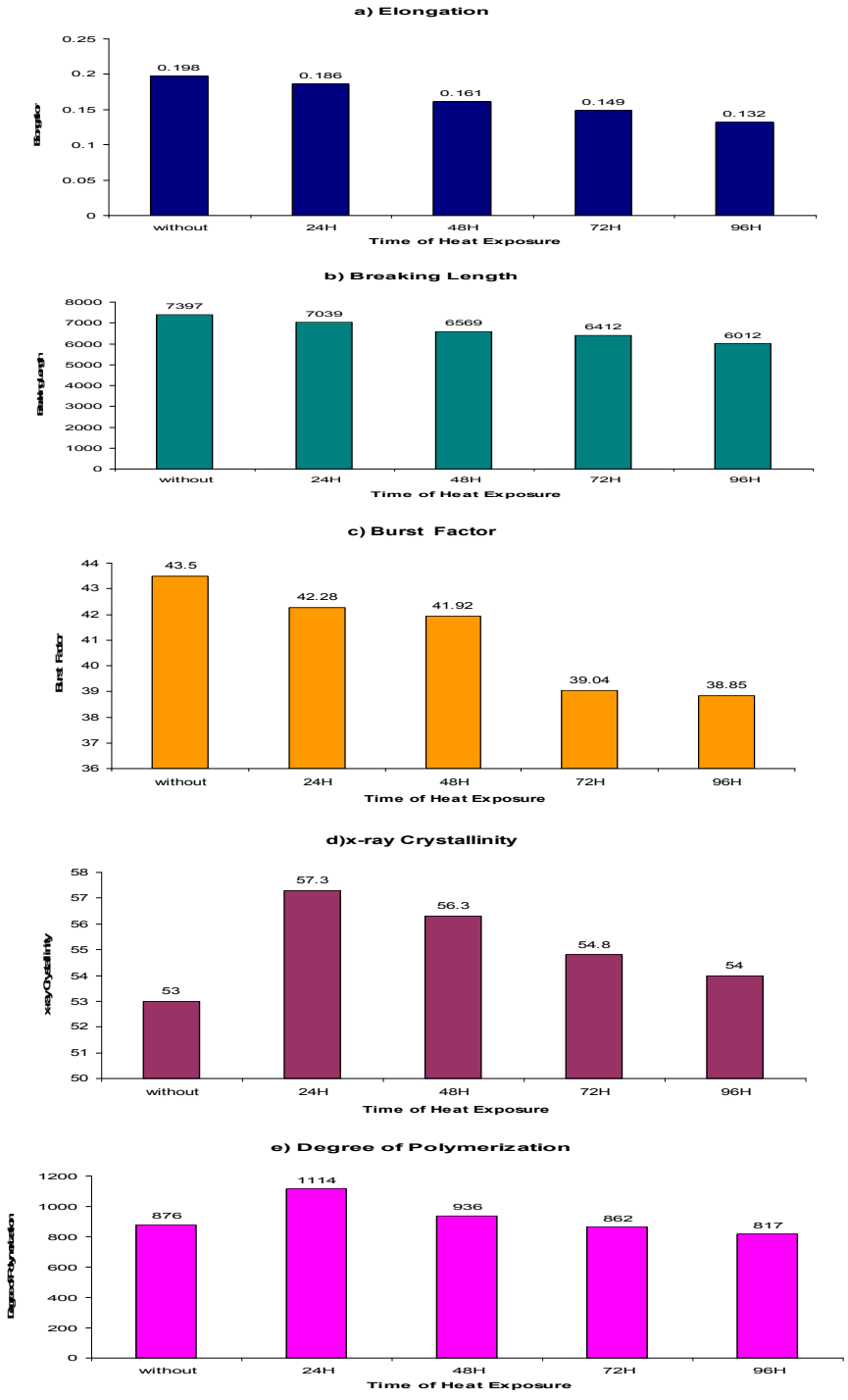


Fig. 3: Physical properties of the samples treated with 2 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

3.3. Effect of treatment with 6 % sodium hydroxide and 0.5 % zinc chloride at different time intervals on the physical properties of paper sheets:

The date for variation in physical properties of cellulose samples treated with 6 % sodium hydroxide and 0.5 % zinc chloride then subjected to heat treatment at 100 ^{o}C for different time intervals are represented in table (5) and in fig. (4). From the results obtained, it was found that:

- The elongation percent decreased from 0.231 % for unaged sample to 0.196 % for sample aged for 96 hours. Thus a decrease in the elongation percent of about 15 % was obtained as a result of aging for 96 hours.
- The breaking length also decreased from 5294 m to 4126 m as a result of the same treatment. This indicates that a decrease of about 20 % occurred as a result of the heat treatment at 100 ^{o}C for 96 hours.
- The burst factor also decreased from 33.1 to 29.2 as a result of the same above treatment. So that burst factor loss as about 12 % of its original value as a result of the aging process.
- The X-ray determined crystallinity increased from 50 to 54.6 after treatments for 24 hours then decreased to 51.2 after 96 hours heat treatment.
- The same trend can be also noticed for the degree of polymerization where it increases from 788 to 876 after 24 hours then it began to decrease after that and till reaches the value of 639 after 96 hours of heat treatment.

Table 5: Physical properties of the samples treated with 6 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

NO.	Thermal Treatment	Elongation %	Breaking Length m.	Burst Factor	X–Ray Crystallinity	Degree of Polymerization.
11	without	0.231	5294	33.1	50	788
12	24 hrs	0.225	5179	30.88	54.6	876
13	48 hrs	0.219	4696	30.21	54.3	817
14	72 hrs	0.200	4613	29.50	52	773
15	96 hrs	0.196	4126	29.21	51.2	639

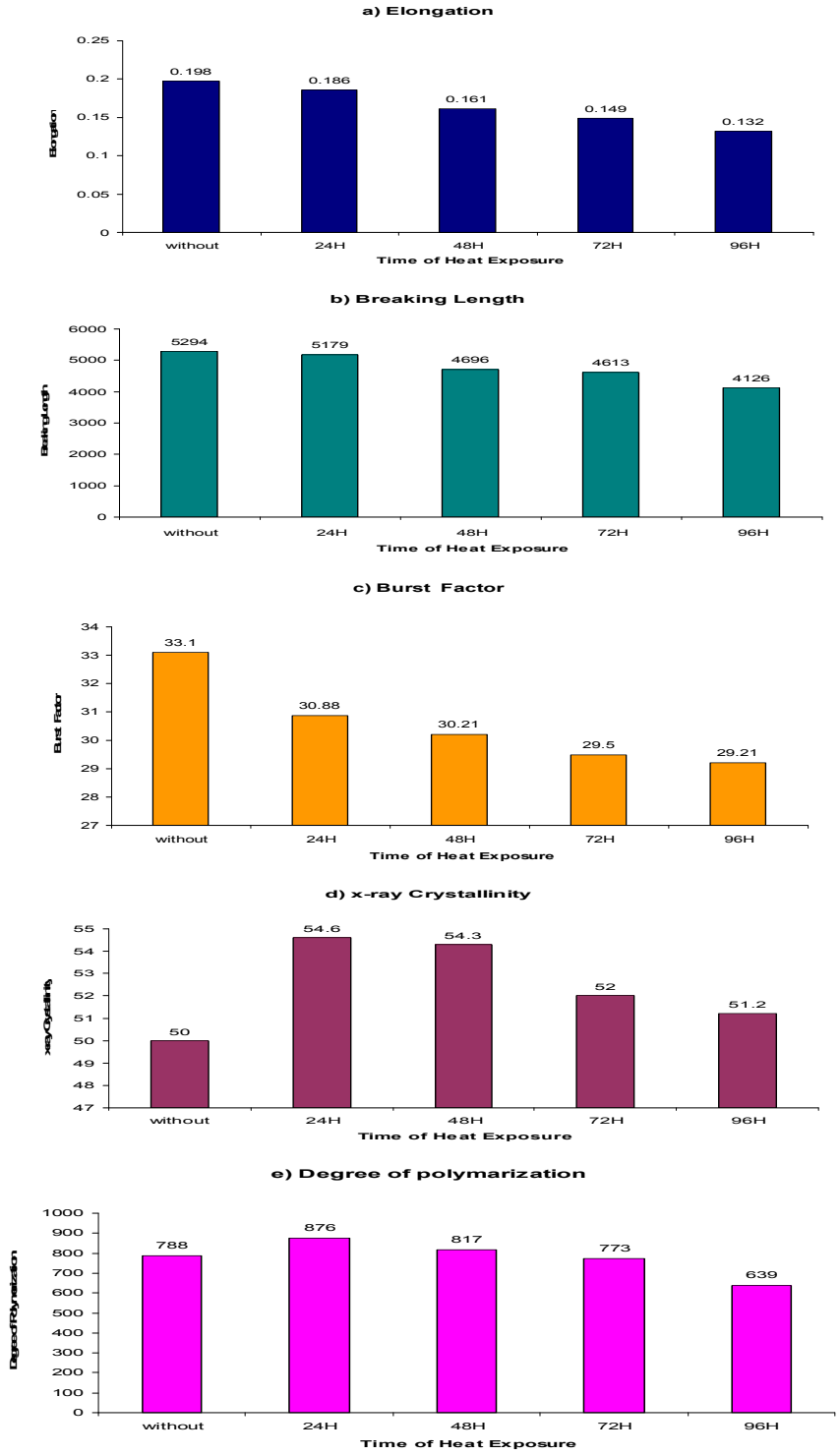


Fig. 4: Physical properties of the samples treated with 6 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

3.4. Effect of treatment with 10 % sodium hydroxide and 0.5 % zinc chloride at different time intervals on the physical properties of paper sheets:

The effect of heat treatment at 100 ^{o}C for the different time intervals up to 96 hrs on the physical properties of refined paper with 10 % sodium hydroxide in presence of 0.5 % zinc chloride was studied. The data are represented in table (6) and in fig. (5). From the results obtained, it was found that:

- The elongation percent decreased from 0.22 % to 0.18 % after 96 hours exposer, this is equivalent to 19 % decrease in the elongation due to the aging for 96 hours.
- The breaking length also decreased from 3954 m to 3065 m as a result of the heat treatment, this represents 33 % total decrease in breaking length.
- The burst factor decreased also from 21.75 to 18.03 as a result of the heat treatment (aging) for 96 hours; this decrease is equivalent to 18 % decrease in this properties.
- Similarly the X-ray determined crystallinity increased from 48 to 52.8 after 24 hours treatment then begined to decrease till it reached 49.2 after 96 hours.
- The same trend was noticed for the degree of polymerization, where it increased from 676 to 824 after 24 hours heat treatment then began to decrease to 528 after 24 hours treatment.

Table 6: Physical properties of the samples treated with 10 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

NO.	Thermal Treatment	Elongation. %	Breaking Length m.	Burst Factor	X –Ray Crystallinity	Degree of Polymerization
16	Without	0.22	3954	21.75	48	676
17	24 hrs	0.215	3747	20.45	52.8	824
18	48 hrs	0.21	3243	19.81	53	765
19	72 hrs	0.186	3122	18.44	49.7	632
20	96 hrs	0.18	3065	18.03	49.2	528

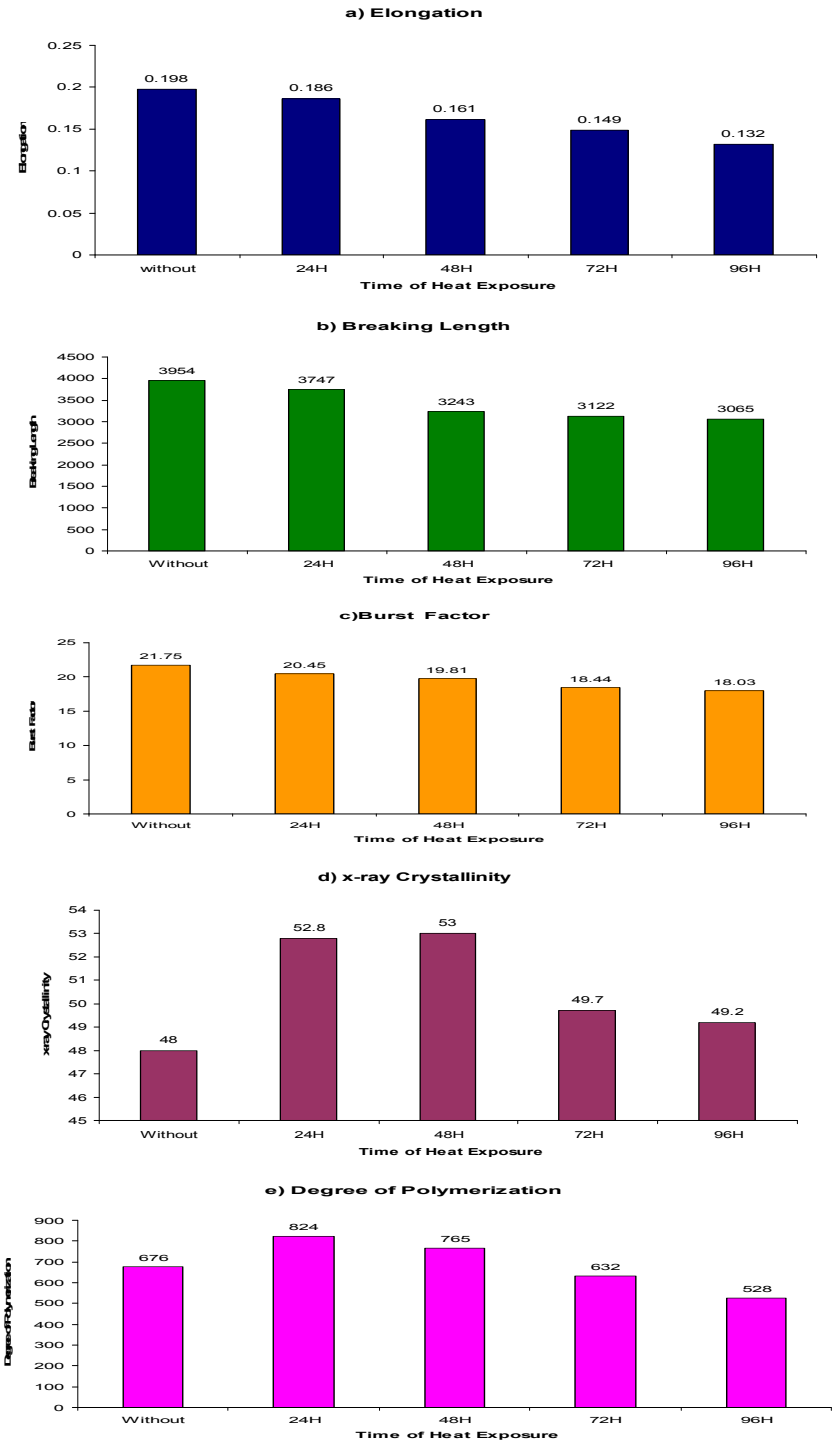


Fig. 5: Physical properties of the samples treated with 10 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

3.5. Effect of treatment with 14 % sodium hydroxide and 0.5 % zinc chloride at different time intervals on the physical properties of paper sheets:

The effect of aging at 100 ^{o}C for time intervals up to 96 hours on the physical properties of the paper sheets treated with 14 % sodium hydroxide and 0.5 % zinc chloride was studied. The data are represented in table (7) and in fig. (6). From the results obtained, it was found that:

- For elongation at break lengths their values decreased as the time of exposure increased, elongation percent of 0.207 % for the blank decreased to 0.165 % for samples treated for 96 hours. The decrease was about 21 % as a result of heat treatment up to 96 hours.
- The breaking length which was 2870 m for the blank decreased to 2342 m for the aged samples for 96 hours. The decrease was about 19 % as a result for the aging.
- Burst factor decreased also by about 14 % as a result of aging for 96 hours. Since it decreased form 14.05 to 12.11.
- X-ray determined crystallinity increased after 24 hours aging from 45.7 to 50.7 as a result of water evaporation which decreases hydrogen bonds in the cellulose chains making it more ordered and hence the X-ray crystallinity increased. The X–ray determined crystallinity decreased after 24 hours gradually due to derange of hydrogen bonds between cellulose chains itself and this gives less ordered cellulose and hence The X–ray determined crystallinity decreased after that.
- The degree of polymerization firstly increased from 594 to 817 after thermal treatment for 24 hours. This is due to that

the newly in accessible regions formed as a result of drying. On the other hand, prolongated thermal treatments from 48 to 96 hours assisted interaction of zinc chloride with free accessible hydrogens of cellulosic fibers loading to degradation of cellulose.

Table 7: Physical properties of the samples treated with 14 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

NO	Thermal Treatment	Elongation %	Breaking Length m.	Burst Factor	X –Ray Crystallinity	Degree of Polymerization.
21	Without	0.207	2870	14.05	45.7	594
22	24 hrs	0.205	2738	13.82	50.7	817
23	48 hrs	0.186	2470	13.56	49.7	772
24	72 hrs	0.171	2431	13.19	48	624
25	96 hrs	0.165	2342	12.11	46.7	579

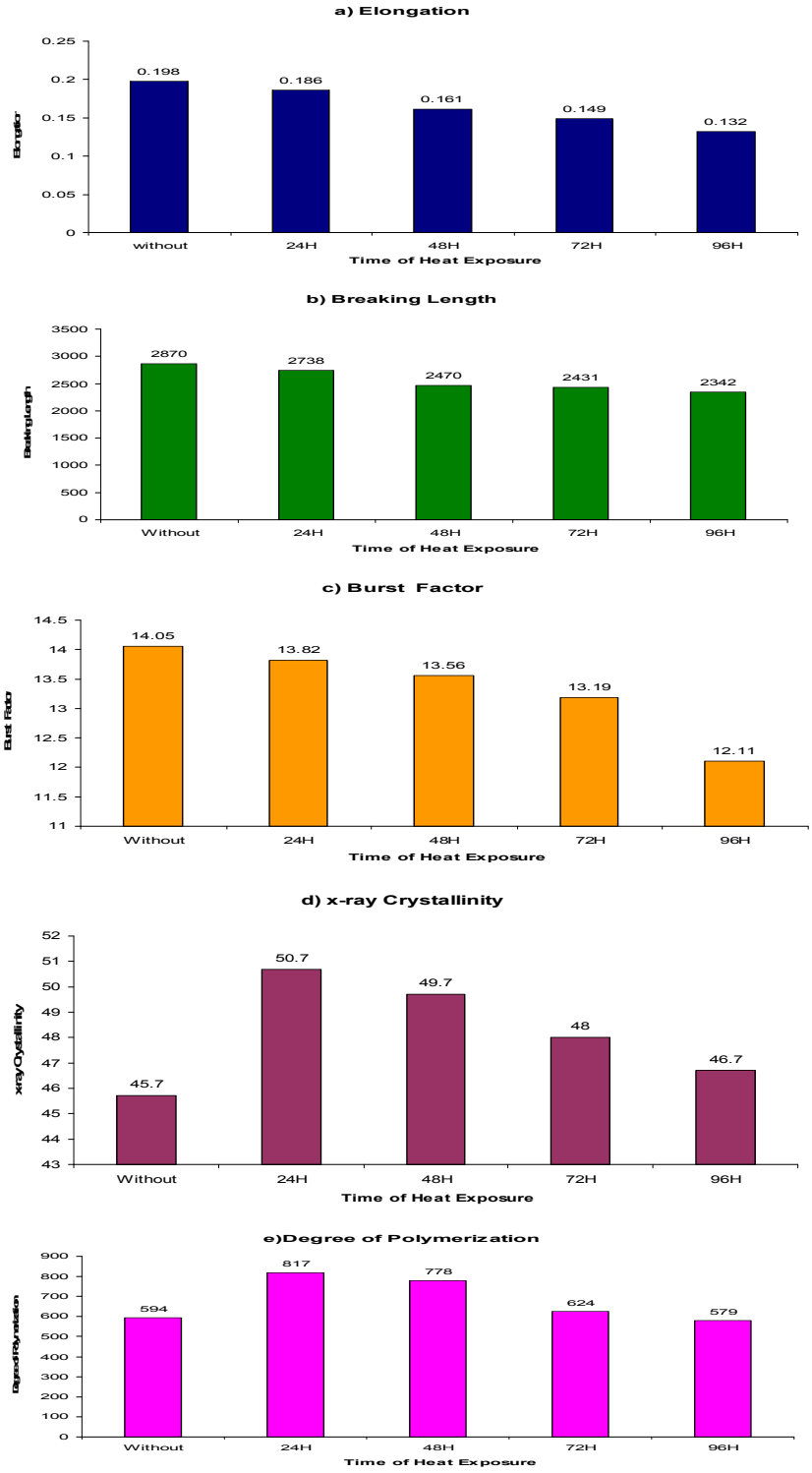


Fig. 6: Physical properties of the samples treated with 14 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

3.6. Effect of treatment with 18 % sodium hydroxide and 0.5 % zinc chloride at different time intervals on the physical properties of paper sheets:

The effect of aging at 100 ^{o}C for time intervals up to 96 hrs on the physical properties treated with 18 % sodium hydroxide and 0.5 % zinc chloride was studied. The data are represented in table (8) and in fig. (7). From the results obtained, it was found that:

- For elongation at break length, their values decreased as the time of exposure increased, elongation percent decreased from 0.128 % for the untreated sample to 0.132 % for the sample treated for 96 hours. This decrease amounted to 33 %.
- In a similar trend, the breaking length decreased from 2076m in case of the untreated sample to 1319 m after treated at 100 ^{o}C for 96 hours leading to a total decrease of 37% from its untreated value.
- The burst factor is also decreased by about 31 % for the samples treated for 96 hours. The blank burst factor was 7.99, this value decreased to 5.56 for the treated samples for 96 hours.
- The X –ray determined crystallinity index increased firstly from 43.1 to 48.7 after 24 hours treatment then decreased with the increase of aging time to 42.6 after 96 hours aging.
- The degree of polymerization which was 572 for the blank sample (unaged sample), it increases at first after 24 hours to 779 then decreased with increasing the aging time to 439 after 96 hours aging.

Table 8: Physical properties of the samples treated with 18 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

NO	Thermal Treatment	Elongation %	Breaking Length m.	Burst Factor	X –Ray Crystallinity	Degree of Polymerization.
26	without	0.198	2076	7.99	43.1	572
27	24 hrs	0.186	1754	7.82	48.7	779
28	48 hrs	0.161	1613	6.54	47.7	602
29	72 hrs	0.149	1377	6.12	45.7	573
30	96 hrs	0.132	1319	5.56	42.6	439

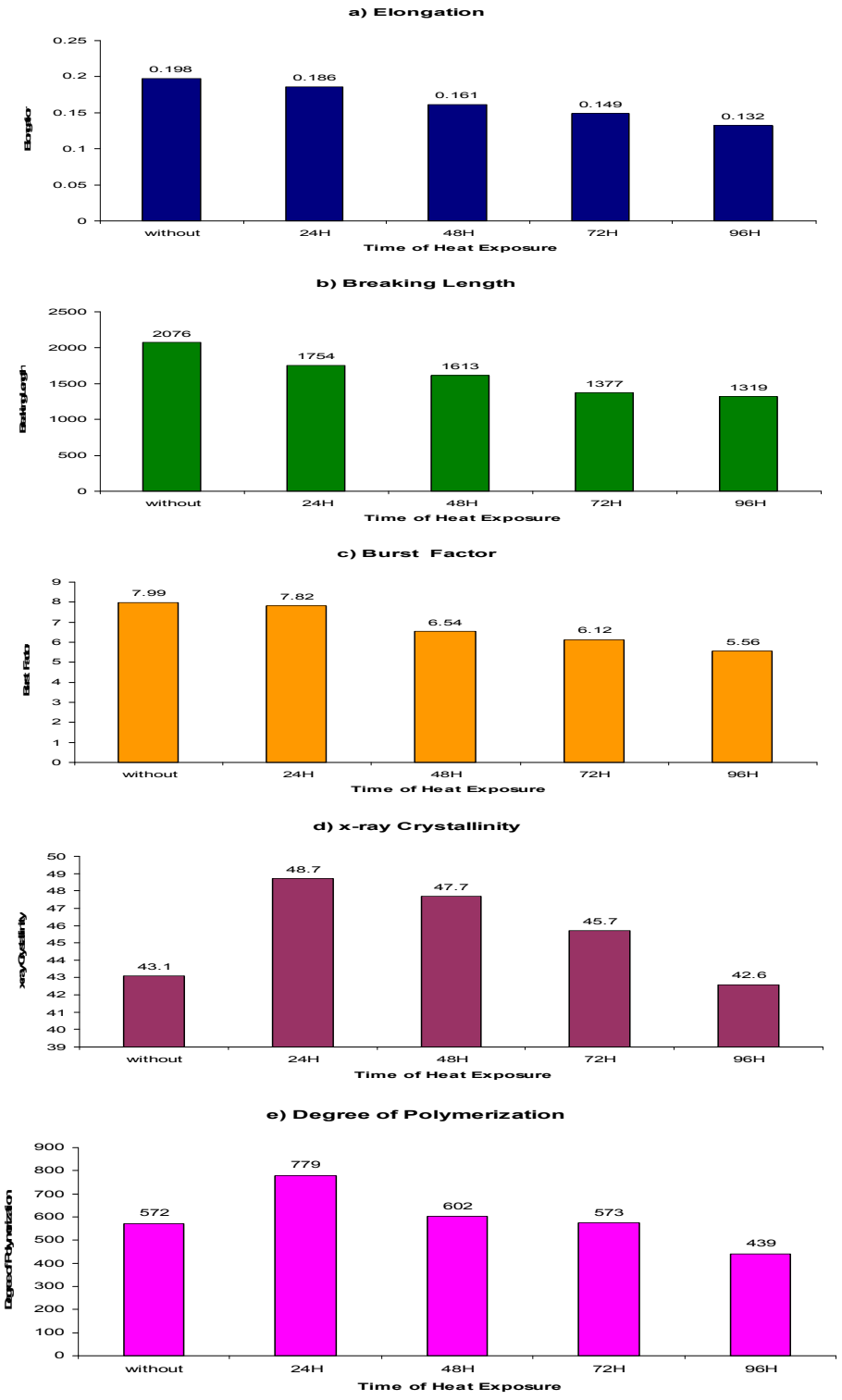


Fig. 7: Physical properties of the samples treated with 18 % sodium hydroxide and 0.5 % zinc chloride at different intervals of thermal treatment

4. Effect of thermal aging and sodium hydroxide concentration on each of the physical properties of paper sheets alone:

4.1. Elongation percent:

The effect of treatment with different concentrations of sodium hydroxide as well as different thermal intervals at 100 ^{o}C on the elongation percent of the paper samples are shown in table (9) and fig.(8). From the numerical data cited in table (9), it is obvious that both two factors have decreasing effect on the elongation percent, but the effect of increasing sodium hydroxide concentration is more effective than that due to times of thermal aging. This can be observed from the horizontal trend in table (9) (effect of concentrations of sodium hydroxide) and the vertical trend (effect of increasing time intervals). From above results, we can conclude that the elasticity of cellulosic fiber become less with increase of both factors.

Table 9: Effect of both sodium hydroxide concentration and aging time on the elongation percent

Conc. of NaOH / Thermal Time	**without**	**2%**	**6%**	**10%**	**14%**	**18%**
Without	0.29	0.246	0.231	0.220	0.207	0.198
24 hrs	0.267	0.230	0.225	0.215	0.205	0.186
48 hrs	0.259	0.224	0.219	0.210	0.186	0.161
72 hrs	0.249	0.210	0.200	0.186	0.171	0.149
96 hrs	0.244	0.207	0.196	0.180	0.165	0.132

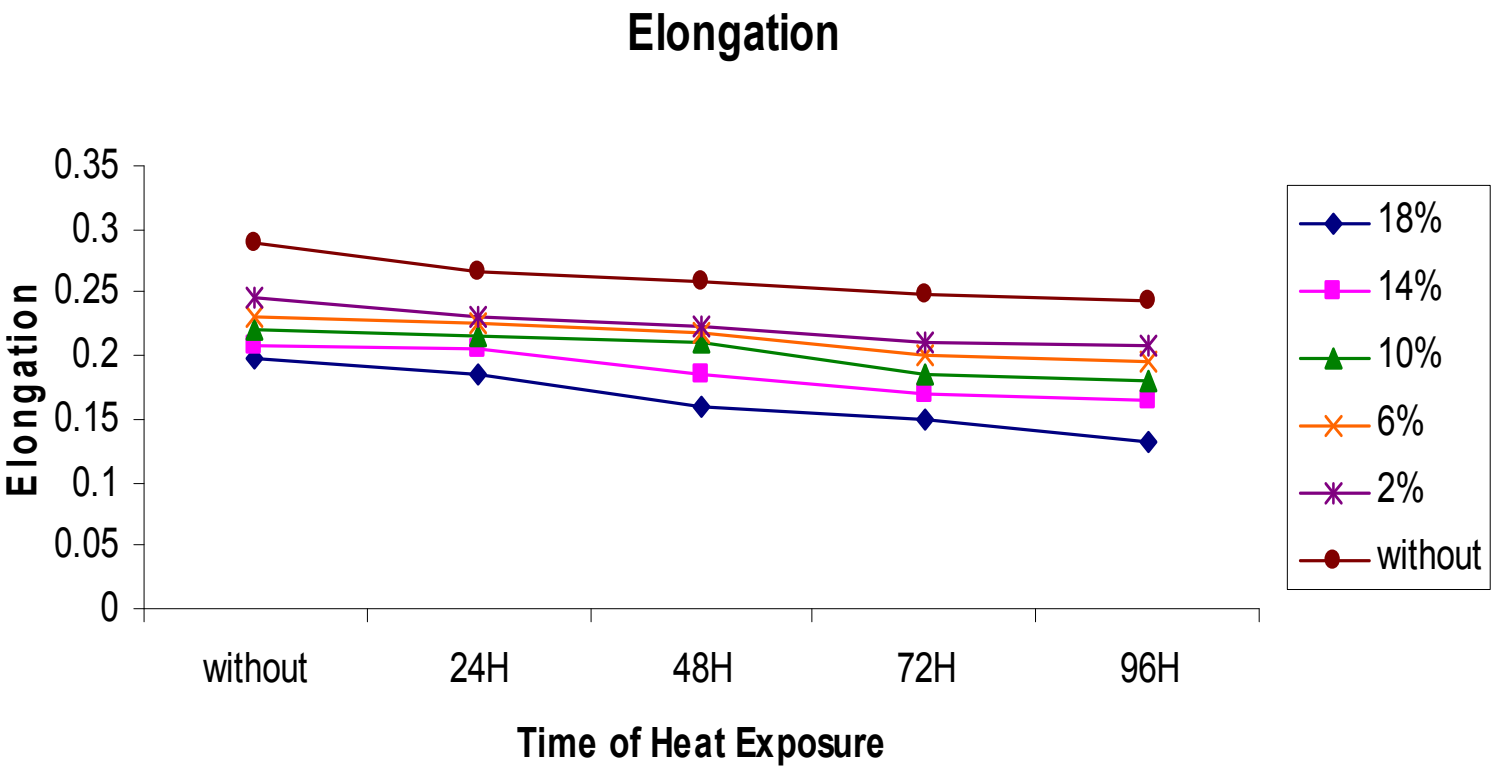


Fig. 8: Effect of both sodium hydroxide concentration and aging time on the Elongation percent

4.2. Breaking Length:

Table 10 and fig. 11 illustrate the effect of both sodium hydroxide concentration and time of aging on the breaking length of paper samples. The data cited in table (10) indicate that:

- At one and the same sodium hydroxide concentration (vertical trend), the breaking length decreased gradually by increasing the time intervals of thermal treatment at 100 ^{o}C.
- At one and the same time interval of thermal treatment (horizontal trend), the breaking length increased by treating with 2 % sodium hydroxide solution.

This can be attributed to the slight refining that takes place for the pulp at 2 % hot sodium hydroxide, where some of the very short molecules of cellulose dissolved which makes the rest of molecule more attached to each other and gives some higher result for unaged and aged samples, But the effect of aging on this sample (2 % sodium hydroxide treated) is similar to other samples and a decrease in the breaking length of about 19 % is observed compared with 13 % for the untreated samples and 37 % for the samples treated with 18 % sodium hydroxide.

Table 10: Effect of both sodium hydroxide concentration and aging time on the breaking length

Conc. of NaOH / Thermal Time	**Without**	**2%**	**6%**	**10%**	**14%**	**18%**
without	6908	7397	5294	3954	2870	2076
24 hrs	6602	7039	5179	3747	2738	1754
48 hrs	6260	6569	4696	3243	2470	1613
72 hrs	6090	6412	4613	3122	2431	1377
96 hrs	5550	6012	4126	3065	2342	1319

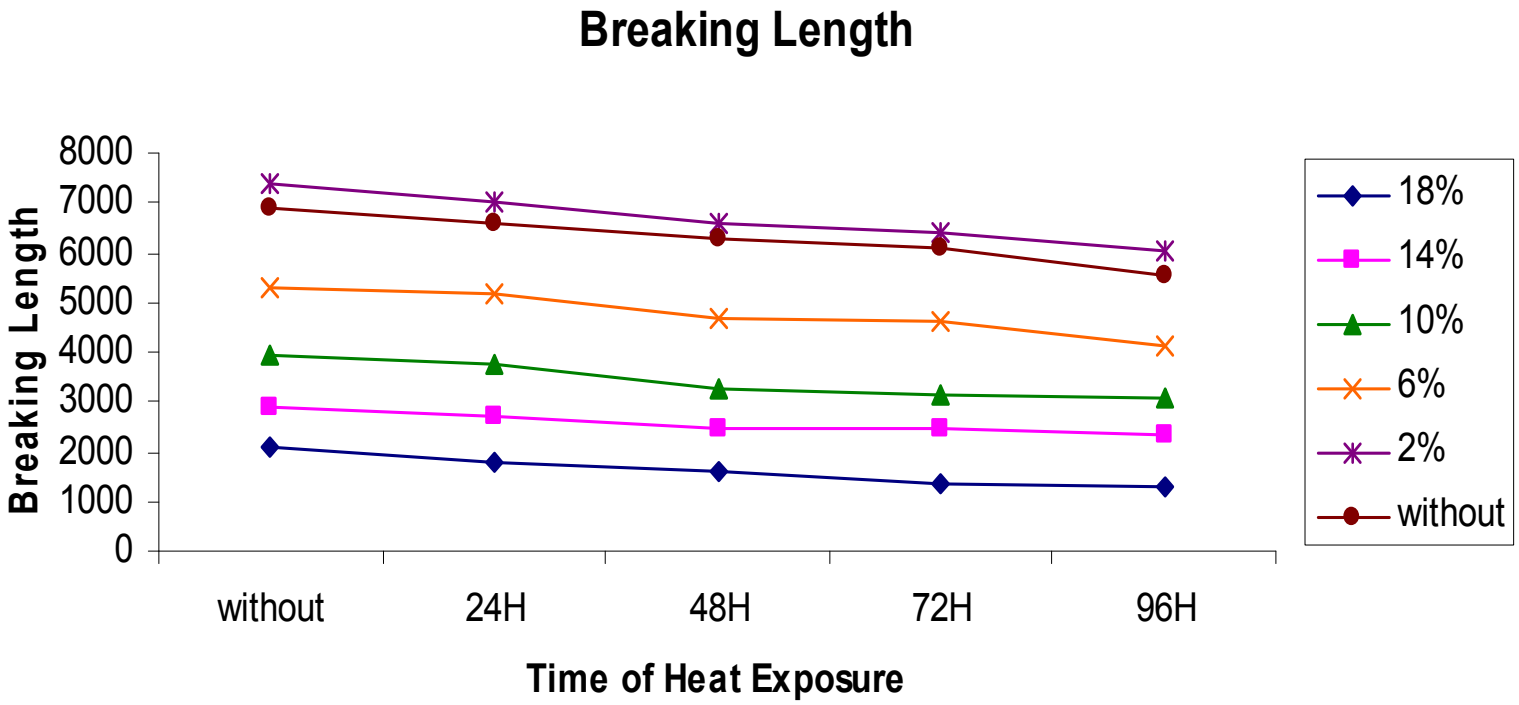


Fig. 9: Effect of both sodium hydroxide concentration and aging time on the breaking length

4.3. Burst Factor:

Table 11 and fig. 10 show the effect of both sodium hydroxide concentration and time of aging on the burst factor. Samples without heat treatment or sodium hydroxide treatment gave a burst factor of about 51.28, whereas samples treated with 18 % sodium hydroxide and aged for 96 hours gave only 5.56 burst factor. We can say that this sample lost about 90 % of its burst factor as a result of both sodium hydroxide treatment and aging for 96 hours. Also we can see that samples without sodium hydroxide treatment lost about 14 % of its original burst factor as a result of aging for 96 hours. Samples treated with 2 % sodium hydroxide loss about 11 % only of its burst factor by aging. By increasing sodium hydroxide concentration, the effect of aging become clearer until it reaches 31 % at sodium hydroxide concentration of 18 %. From the above results, we can conclude that treating the pulp with 2 % sodium hydroxide solution gave the least effect on the burst factor during the aging process.

Table 11: Effect of both sodium hydroxide concentration and aging time on the burst factor

Conc. of NaOH / Thermal Time	**without**	**2%**	**6%**	**10%**	**14%**	**18%**
without	51.28	43.5	33.1	21.75	14.05	7.99
24 hrs	48.62	42.28	30.88	20.45	13.82	7.82
48 hrs	47.71	41.92	30.21	19.81	13.56	6.54
72 hrs	44.84	39.04	29.5	18.44	13.19	6.12
96 hrs	44.39	38.85	29.21	18.03	12.11	5.56

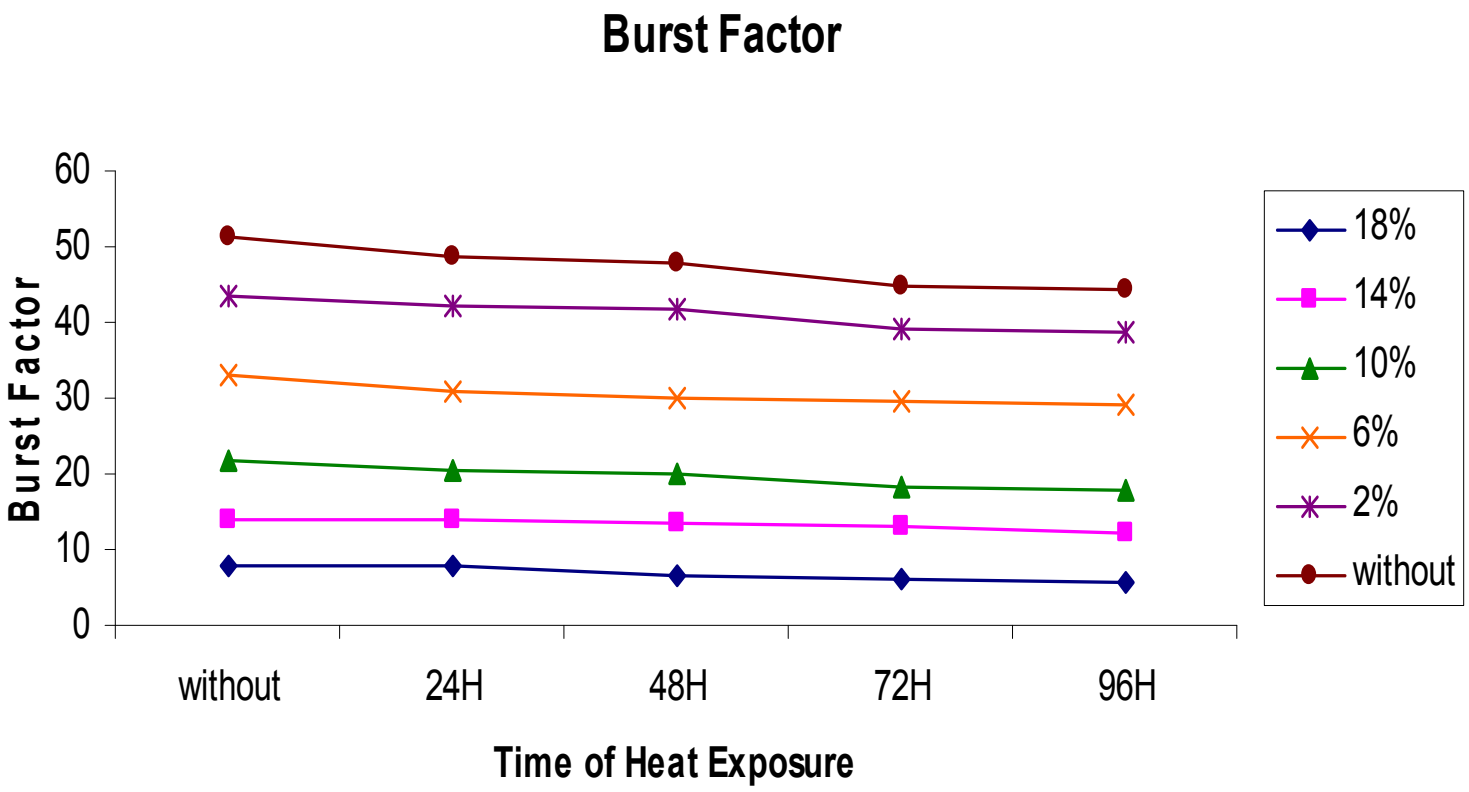


Fig. 10: Effect of both sodium hydroxide concentration and aging time on the burst factor

4.4. X-ray determined Crystallinity:

Table 12 and fig. 11 illustrate the X-ray determined crystallinity for the samples treated with different concentration of sodium hydroxide and different aging time by X-ray method.

Table 12: Effect of both sodium hydroxide concentration and aging time on the X-ray crystallinity

Conc. of NaOH / Thermal Time	**without**	**2%**	**6%**	**10%**	**14%**	**18%**
without	54.6	53	50	48	45.7	43.1
24 hrs	60.4	57.3	54.6	52.8	50.7	48.7
48 hrs	62.6	56.3	54.3	53	49.7	47.7
72 hrs	64	54.8	52	49.7	48	45.7
96 hrs	65.8	54	51.2	49.2	46.7	42.6

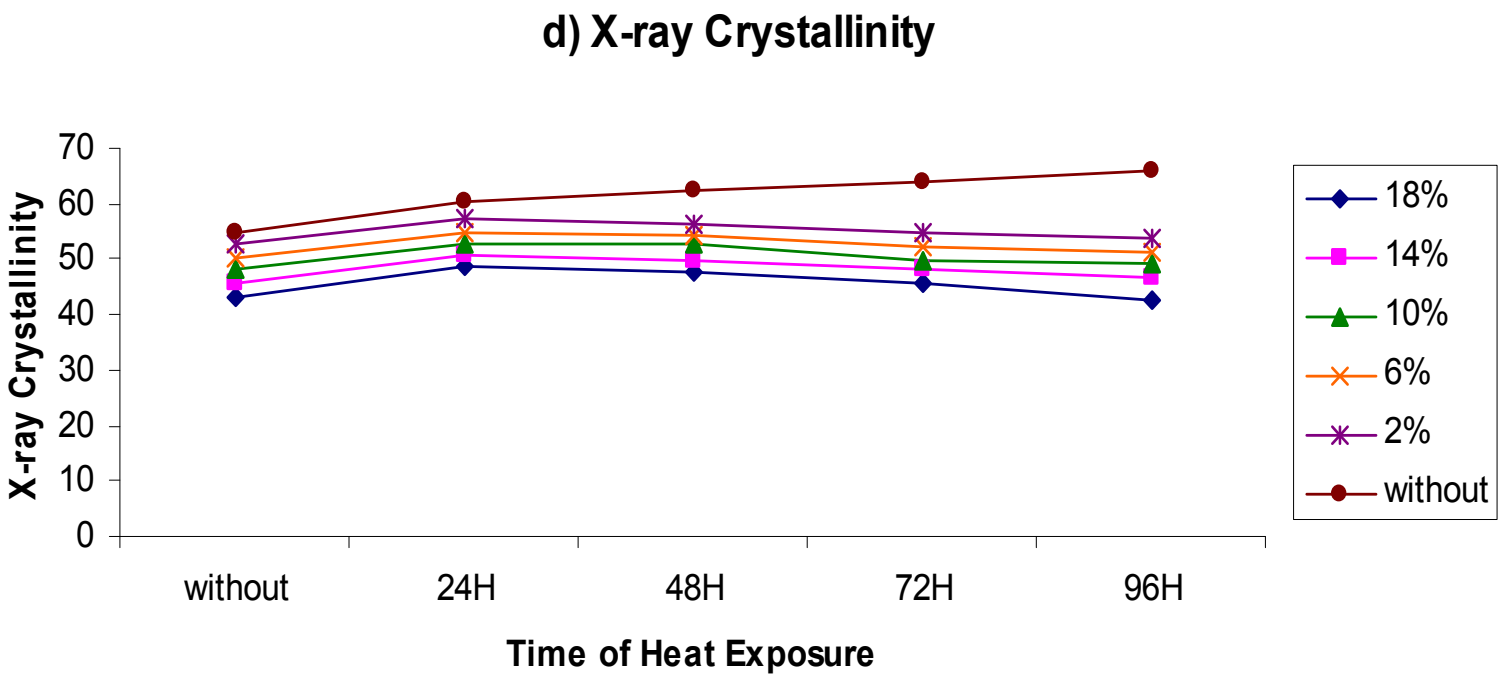


Fig. 11: Effect of both sodium hydroxide concentration and aging time on the x-ray crystallinity

X-ray diffraction pattern

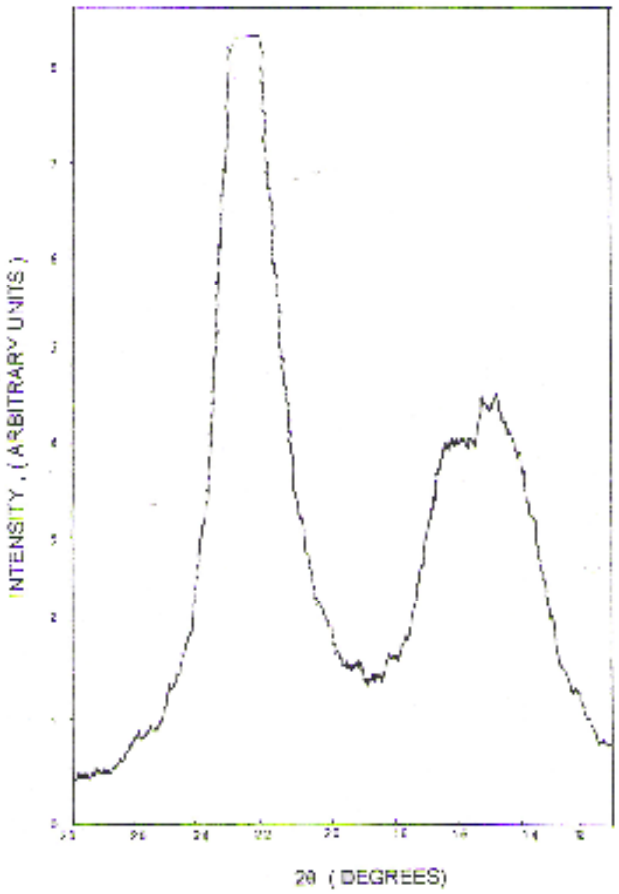


Fig. 12: X-ray diffraction pattern

Fig. 12 shows the X-ray diffraction pattern of the blank sample (bleached wood pulp). For samples which were not treated with sodium hydroxide, the X-ray determined crystallinity increased from 54.6 for the original sample to 65.8 for samples aged for 96 hours. This can be due to the increased ordered cellulose chains produced as a result of treatment. The treatment with sodium hydroxide for the original sample give less ordered structure as the concentration increased. The untreated sample gave crystallinity of 54.6; whereas the sample treated with 18 % sodium hydroxide gave 42.6 X-ray determined crystallinity. That is about 25 % decrease in the X-ray determined crystallinity occurred due to sodium

hydroxide treatment. X-ray determined crystallinity for the treated samples with sodium hydroxide slightly decreased (or increased), due to aging of the samples treated of 96 hours. (from 2-6 %).

As generally known, crystallinity degree of polymers is determined by X-ray radiography, which is completely different from the value obtained by spectrophotometry. However, the mercerization process was evaluated by spectrophotometric method which is more useful in examining structural changes in cellulose.

Degree of Polymerization:

The effects of sodium hydroxide concentration and thermal aging at 100 ^{o}C for different time intervals are recorded in table (13) and shown in fig. (13). Inspection of the data obtained shows that the degree of polymerization for the blank sample increased from 914 to 1180 as a result of heat treatment at 100 ^{o}C for 96 hours, this is due to the increase in crystallinity and the possible aggregation of hemicellulose molecules with themselves or with cellulose chains. In case of the samples treated with 2 % sodium hydroxide some of the hemicellulose molecules are removed and so the heat treatment effect was observed at 24 and 48 hours, where the degree of polymerization increased to 1114 at 24 hours treatment then decreased to 936 after 48 hours heat treatment. At 72 hours treatment nearly the same value as the blank was obtained while at 96 hours the degree of polymerization decreased to 818. On increasing the sodium hydroxide concentration more and more hemicellulose molecules are removed from the sample and the effect of heat treatment tends to decrease the degree of polymerization sharply. For the samples treated with 18 % sodium hydroxide and thermal aging at 100 ^{o}C for 96 hours, the degree of polymerization loses were more than 50 % of its original value. This is in agreement also with the mechanical properties of the treated samples.

Table 13: Effect of both sodium hydroxide concentration and aging time on the degree of polymerization

Conc. of NaOH / Thermal Time	**without**	**2%**	**6%**	**10%**	**14%**	**18%**
without	914	876	788	676	594	572
24 hrs	986	1114	876	824	817	779
48 hrs	1035	936	817	765	772	602
72 hrs	1106	862	773	632	624	573
96 hrs	1179	817	639	528	579	439

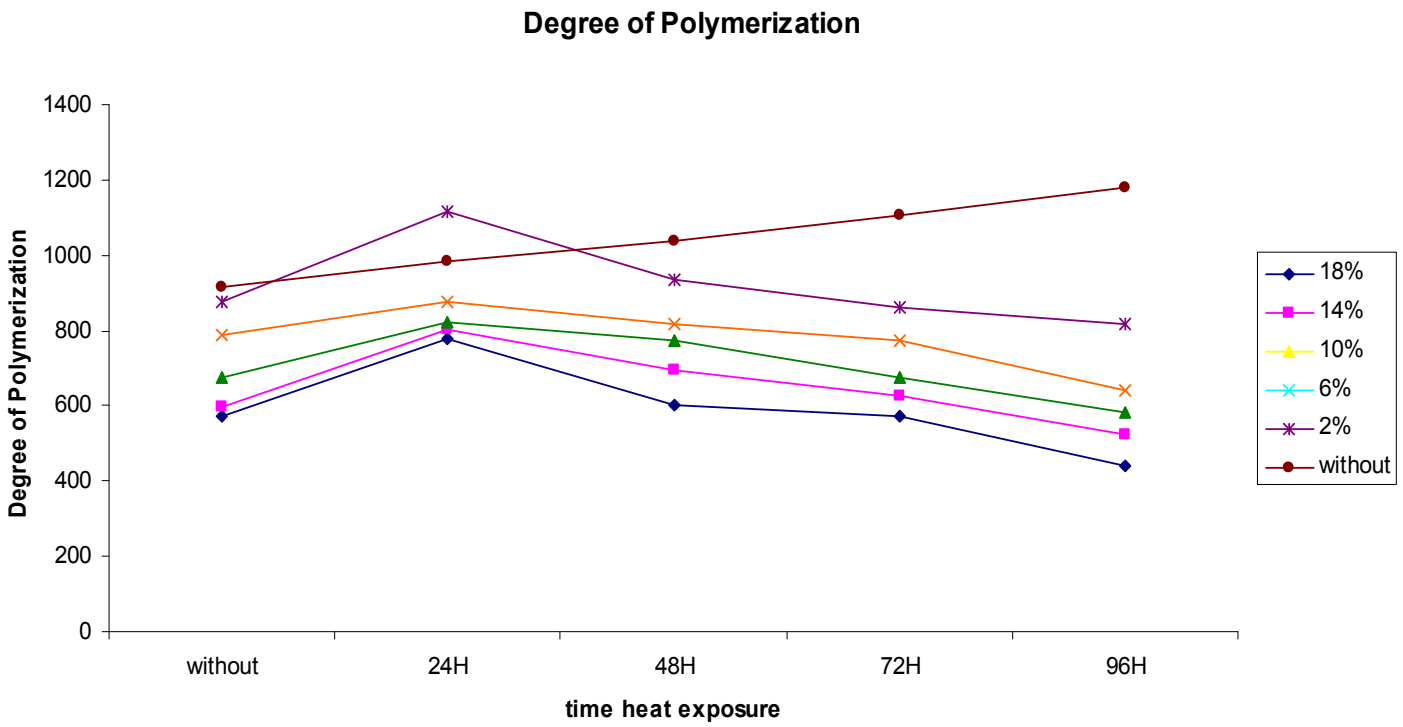


Fig. 13: Effect of both sodium hydroxide concentration and aging time on the degree of polymerization

5. Infrared spectra:

The infrared spectrum is characteristic for the entire molecule. It is known that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic bands that permit us to obtain useful structural information by simple analysis of the spectrum and reference to generalized charts of the characteristic group's frequency.

The infrared absorption spectra of all treated samples were recorded within the range 4000- 500 cm^{-1} using KBr technique. The absorption infrared spectra are shown in figs. (14-19).

The extremely broad absorption band within the region 3400 to 2400 cm^{-1} is characteristic to the OH groups. The broadness of this band increases as the extent of hydrogen bonding increases. The absorptions of the stretching vibrations of the C-H group are obscured being found within this range. This band can be used to measure the total OH content.

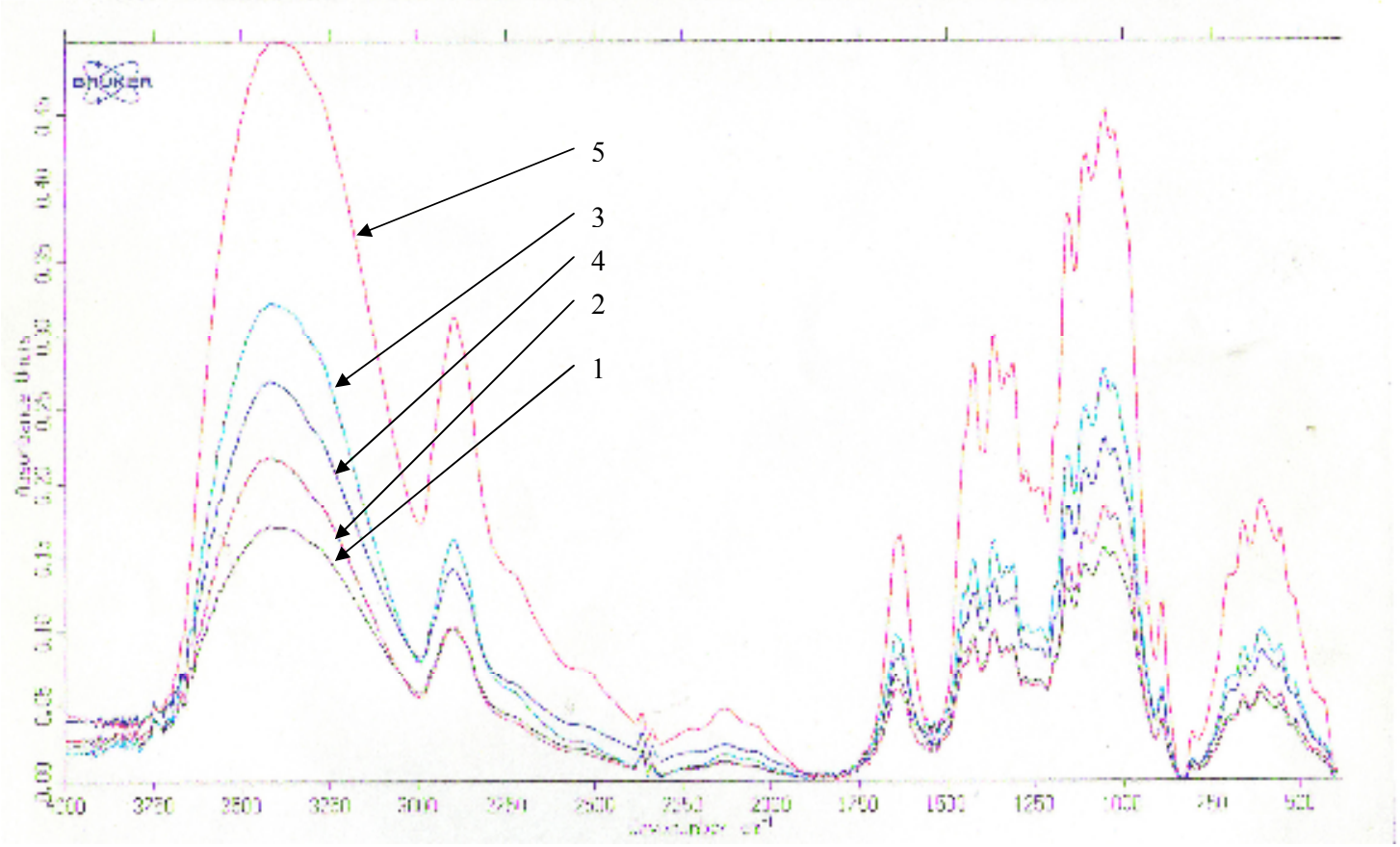


Fig.14: IR spectrum of samples (1-5)

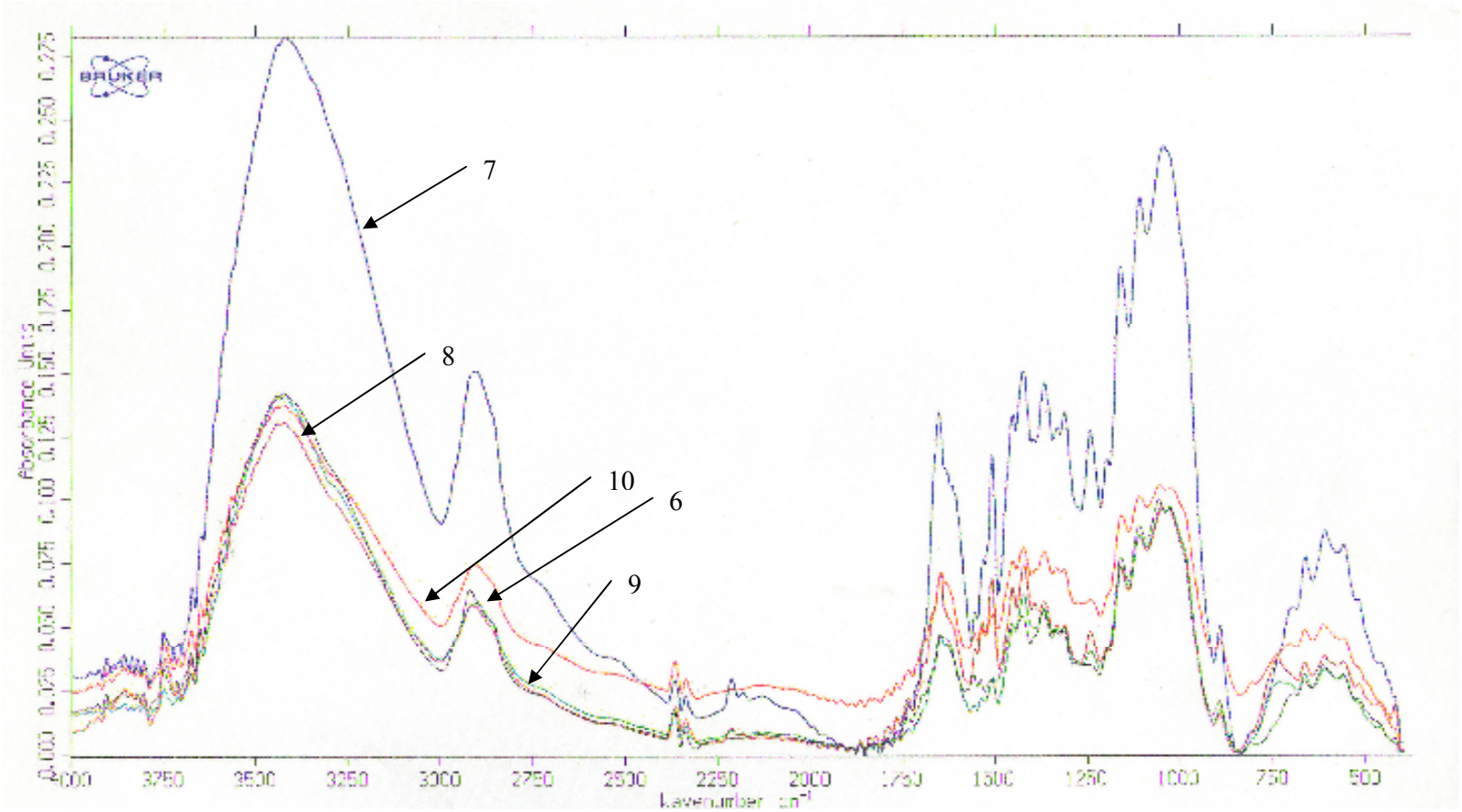


Fig.15: IR spectrum of samples (6-10)

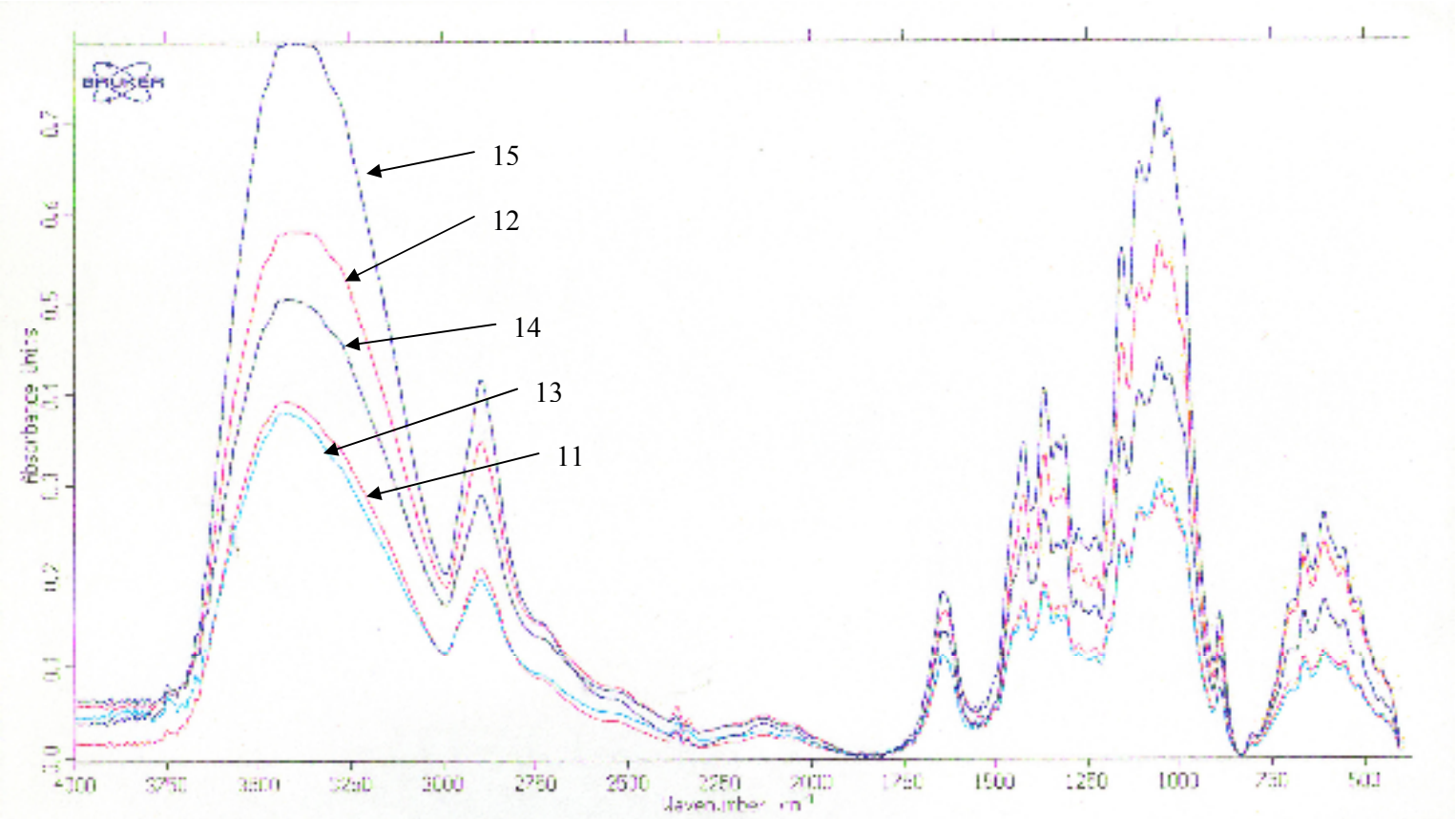


Fig.16: IR spectrum of samples (11-15)

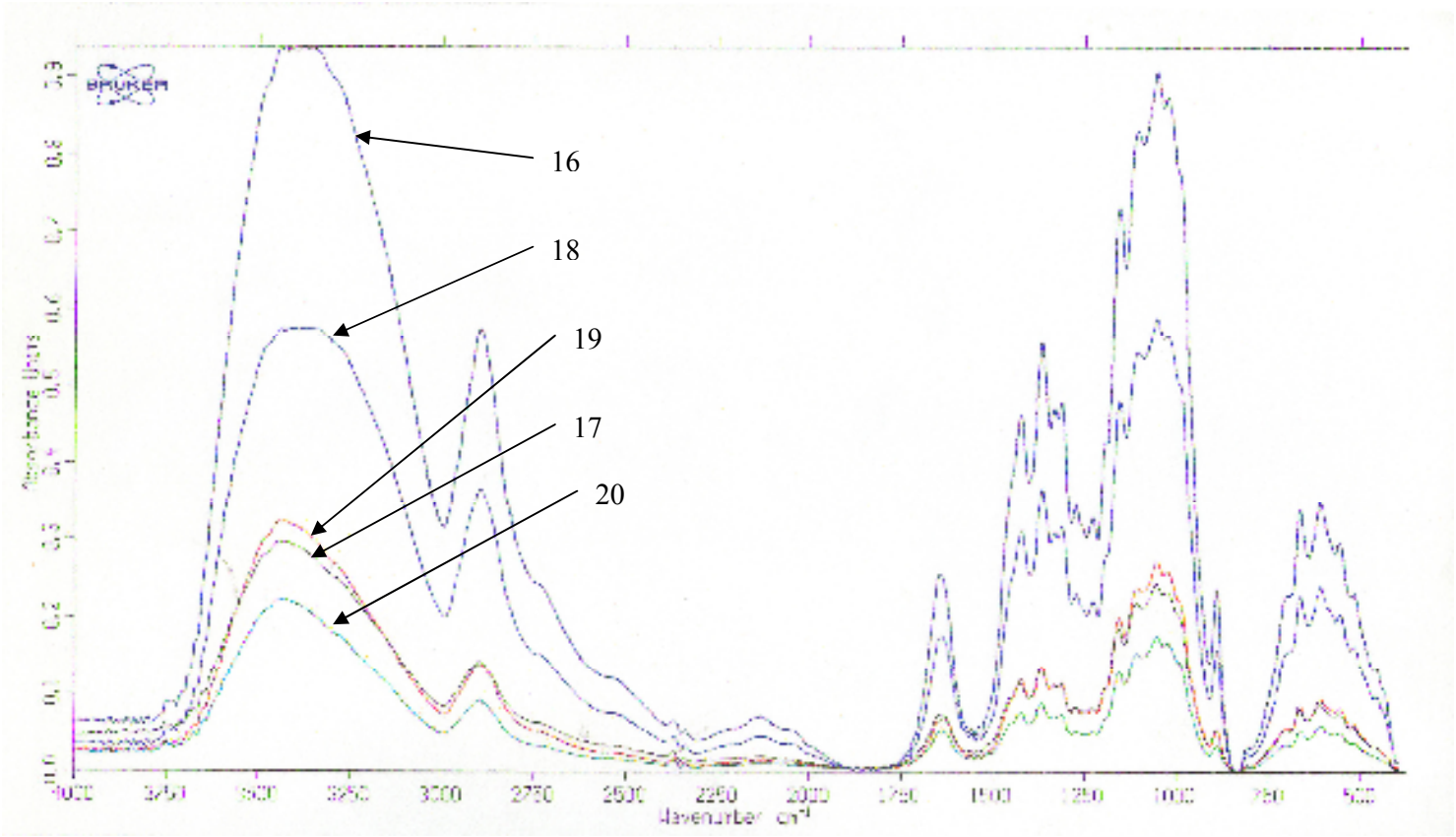


Fig.17: IR spectrum of samples (16-20)

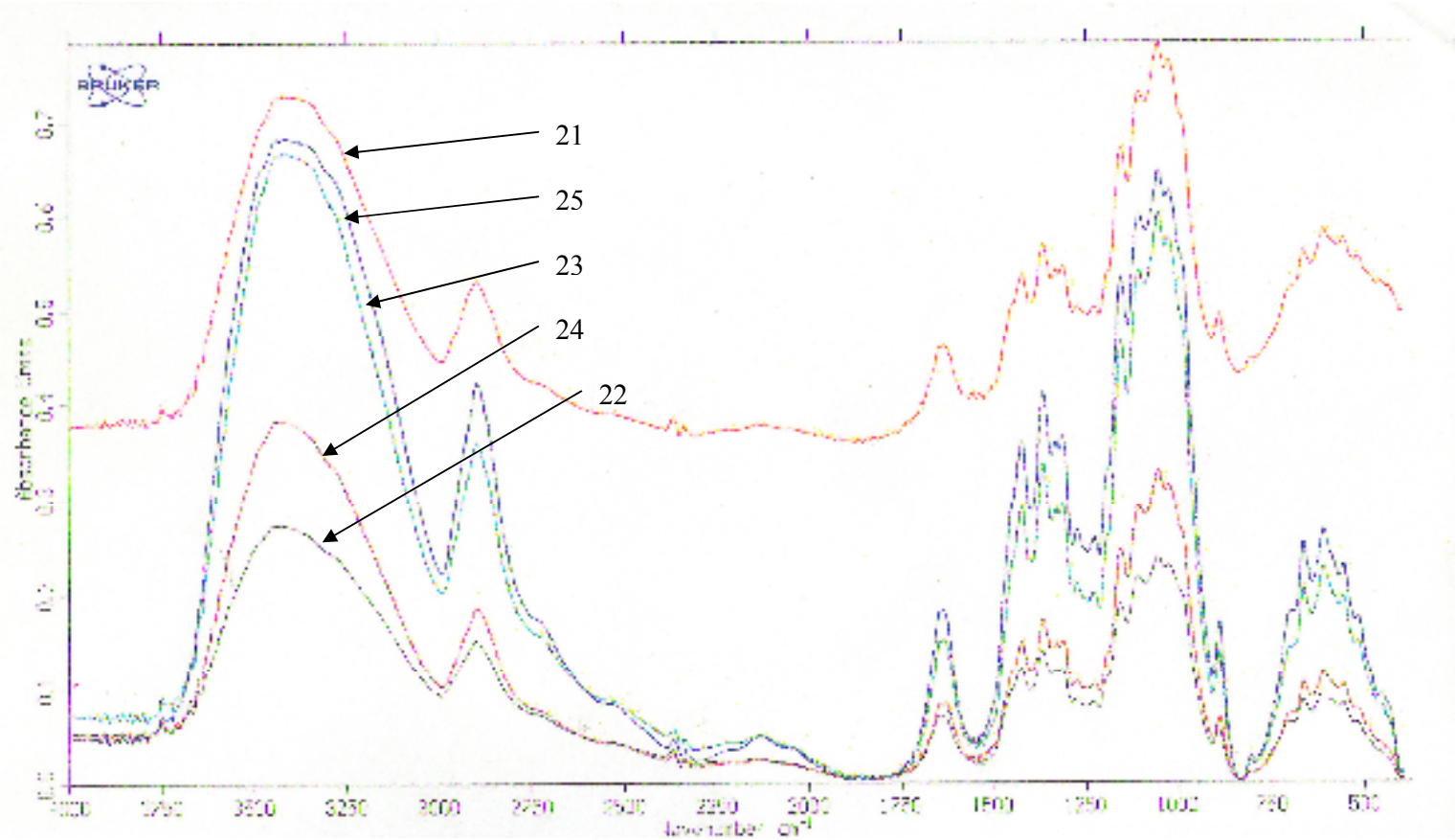


Fig.18: IR spectrum of samples (21-25)

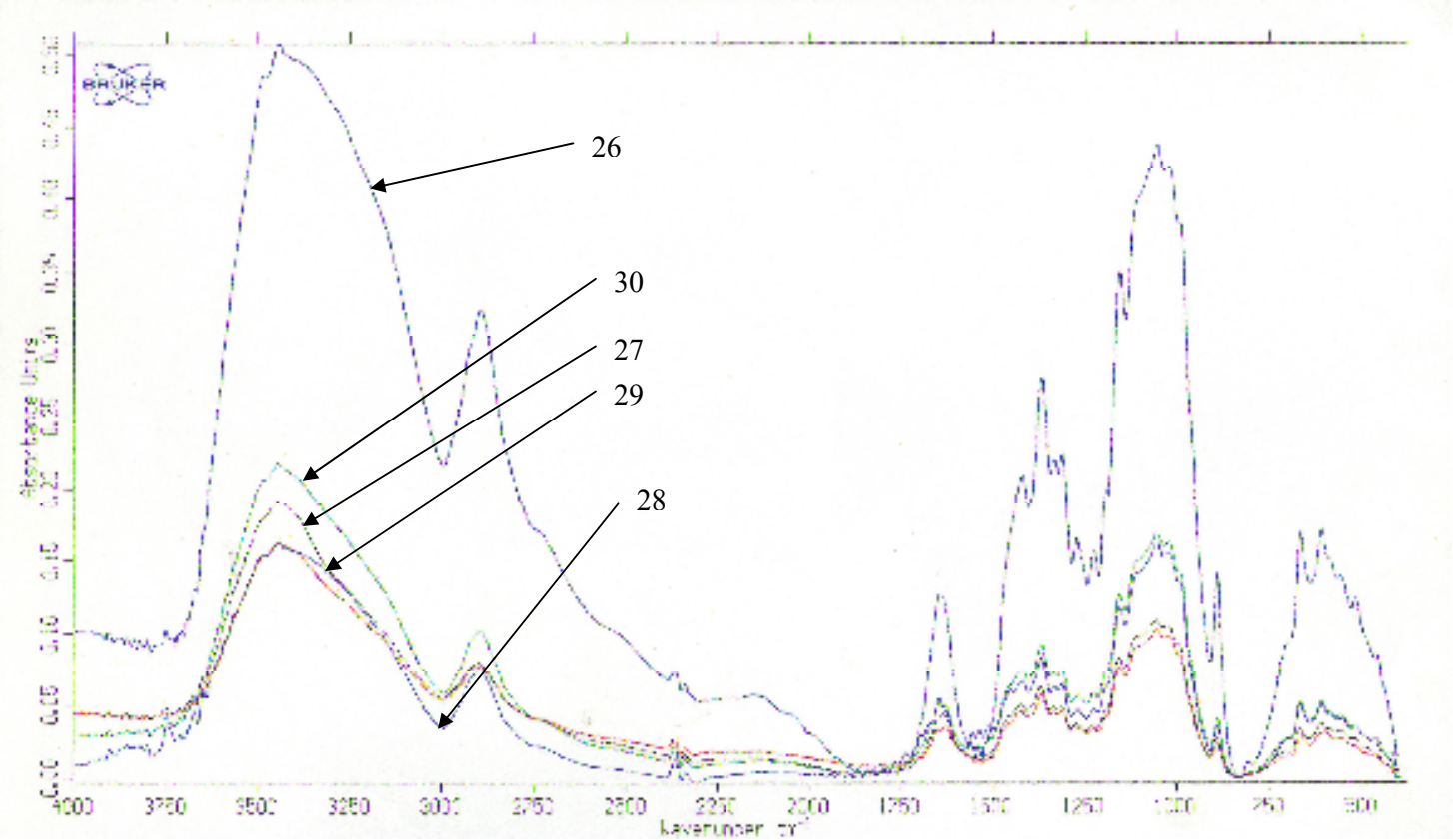


Fig.19: IR spectrum of samples (26-30)

The IR spectral bands of cellulosic material are relatively diffuse because of the high molecular weight. So, to follow the change of the molecular structure of the cellulose, the use of relative absorbance (ratio of any band intensity / band intensity at 1325 cm^{-1}) [125] is more correct than the use of changes that takes place for characteristic band. Also, infrared spectra can give us an idea on the crystallinity of cellulose by calculating the ratio of band intensity at 1425 cm^{-1} which is characteristic of CH vibration of crystallinity region to band intensity characteristic of the CH vibration of amorphous region at 900 cm^{-1}. Thus, crystallinity index is an IR parameter that gives information about the ratio of crystalline region to amorphous region. The parameter was measured according to the absorbance ratio A_{1430}/A_{900} [126].

Besides the measuring of the crystallinity index, the mercerization depth which occurs by swelling of cellulose by sodium hydroxide can also be determined. The mercerization depth gives us a good idea about swelling of cellulose and its decrystallizition. It can be measured by using the ratio of band intensity at 1371 cm^{-1} to band intensity at 1325 cm^{-1}. Cellulose was mercerized in aqueous solution. Results of cellulose mercerizing were determined by IR spectra. Degree of crystallinity of cellulose was determined by A_{1429} /A_{893} and mercerization depth from A_{1375} / A_{1325} [127]. Due to the treatment of cellulose pulp with sodium hydroxide and heating, some degradation and oxidation of OH group can occur. The relative absorbance of OH group at 3425 cm^{-1} decreased due to the oxidation to COOH. So, a new band appeared at 1715 cm^{-1} which characteristic of C=O of carbonyl group. On the other hand, the relative absorbance of C-O-C band at 1114 cm^{-1} which is characteristic of the (1-4) β-O-glucosidic linkage decreased due to the degradation of cellulose chains which occurred by sodium hydroxide solution and heating.

On mercerization many processes take place, e.g. swelling with some exothermic effect and dissolution of hemicellulose as a non-fiber forming components. Because degradation of cellulose occurs to a slight extent, an addition compound of cellulose and sodium hydroxide is formed and intermolecular hydrogen bonds become loose. This phenomenon brings about structural changes in cellulose which depends on sodium hydroxide concentration. The extent of mercerization is affected by some inorganic and organic compounds such as zincate, aluminate or urea.

The treatment of cellulose with sodium hydroxide causes an effect on the molecular structure of cellulose. This change of molecular structure can be followed by infrared spectroscopy. The main parameters affected by treatment of cellulose with sodium hydroxide are crystallinity index, swelling of cellulose chain (related to the measurement of mercerization depth), intensities of OH groups, C=O band (which was related to COOH at 1715 cm^{-1}) and CHO at 1654 cm^{-1}, and the intensity of ether linkage which bonds the glucose molecule (1-4) β-O-glucosidic links.

Crystallinity indeces:

Crystallinity indeces were measured from the infrared spectral data. The value of crystallinity indeces at different thermal aging intervals and different concentrations of sodium hydroxide (2-18 %) are given in table (14) and shown in fig. (20). Measurements showed that crystallinity indeces of cellulose decreased by increasing sodium hydroxide concentration. This is due to swelling of cellulose chains in which the hydrogen bonds between chains decreased, and consequently the amorphous region decreased.

From the table it is seen also that the crystallinity indeces decreased by increasing the time of the heating cellulose material at 100 ^{o}C for different time intervals 24-96 hours. This also is attributed to the destruction of hydrogen bonds between cellulose chains which causes an increase in amorphous region.

Table 14: Effect of both sodium hydroxide concentration and aging time on the crystallinity indeces by FTIR

Conc. of NaOH / Thermal Time	**Without**	**2%**	**6%**	**10%**	**14%**	**18%**
without	2.80	2.50	2.35	2.24	2.09	1.98
24 hrs	2.60	2.35	2.24	2.11	1.98	1.89
48 hrs	2.50	2.28	2.17	2.09	1.94	1.82
72 hrs	2.38	2.24	2.12	2.04	1.86	1.76
96 hrs	2.30	2.17	2.10	1.99	1.84	1.70

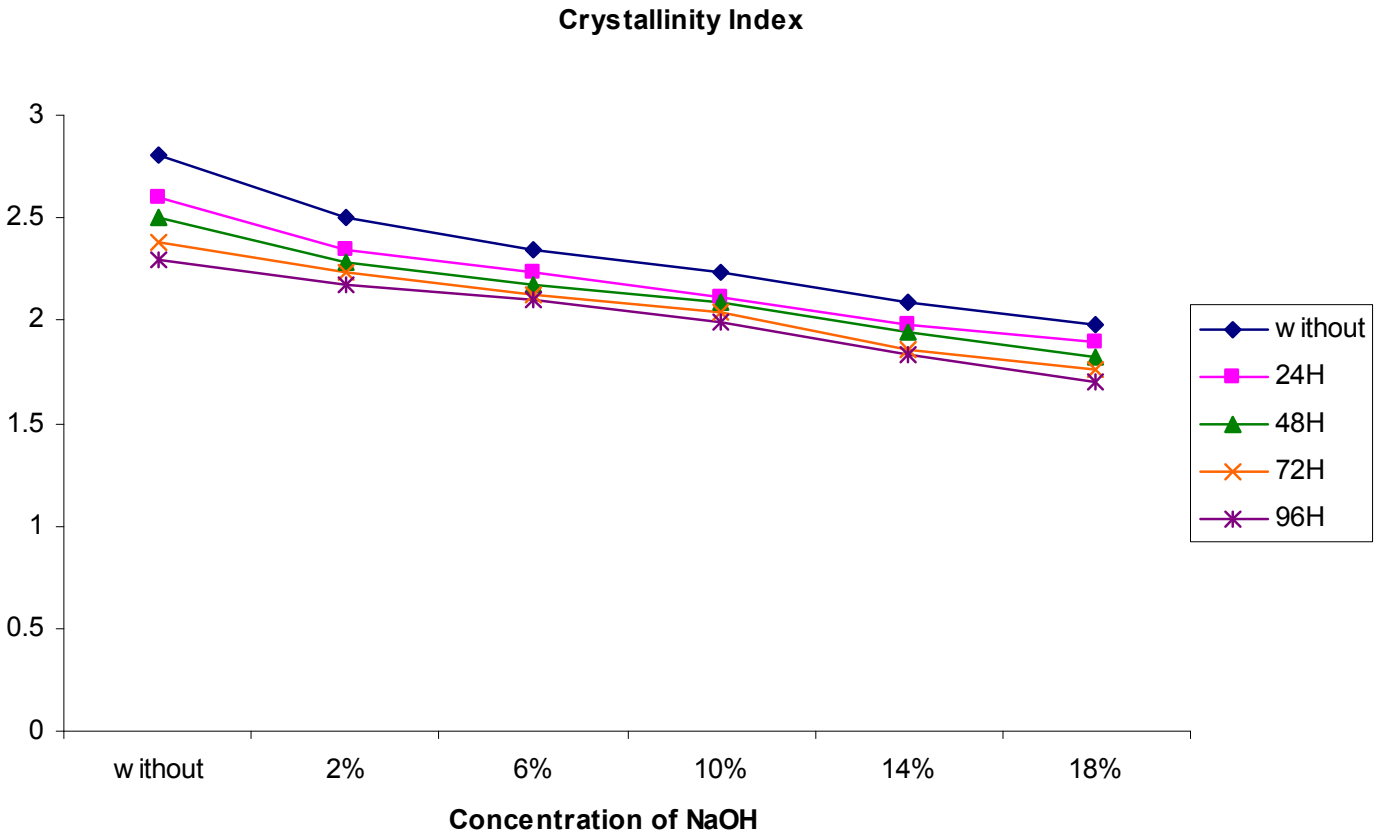


Fig. 20: Effect of both sodium hydroxide concentration and aging time on the crystallinity indeces by FTIR

4.2. Mercerization depth:

The effects of sodium hydroxide concentration (2-18 %) and the time intervals of heat treatment (100 ^{o}C) on the mercerization depth (calculated from infrared spectroscopy) are represented in table (15) and shown in fig. (21). From the data given, it is clear that, the mercerization depth began to increase by increasing sodium hydroxide concentration more than 6 %. Increasing of sodium hydroxide concentration more than 6 % causes the destruction of hydrogen bonds between OH group of cellulose chains and consequently the amorphous regions increases. This is confirmed by the decrease of crystallinity index of cellulose chains by increasing the concentration of NaOH (table 15).

Table 15: Effect of both sodium hydroxide concentration and aging time on the mercerization depth by FTIR

Conc. of NaOH / Thermal Time	**without**	**2%**	**6%**	**10%**	**14%**	**18%**
without	1.100	1.099	1.124	1.184	1.219	1.300
24 hrs	1.047	1.047	1.100	1.160	1.179	1.280
48 hrs	1.004	1.009	1.060	1.124	1.149	1.254
72 hrs	0.973	0.984	1.000	1.094	1.129	1.209
96 hrs	0.933	0.94	0.952	1.047	1.097	1.180

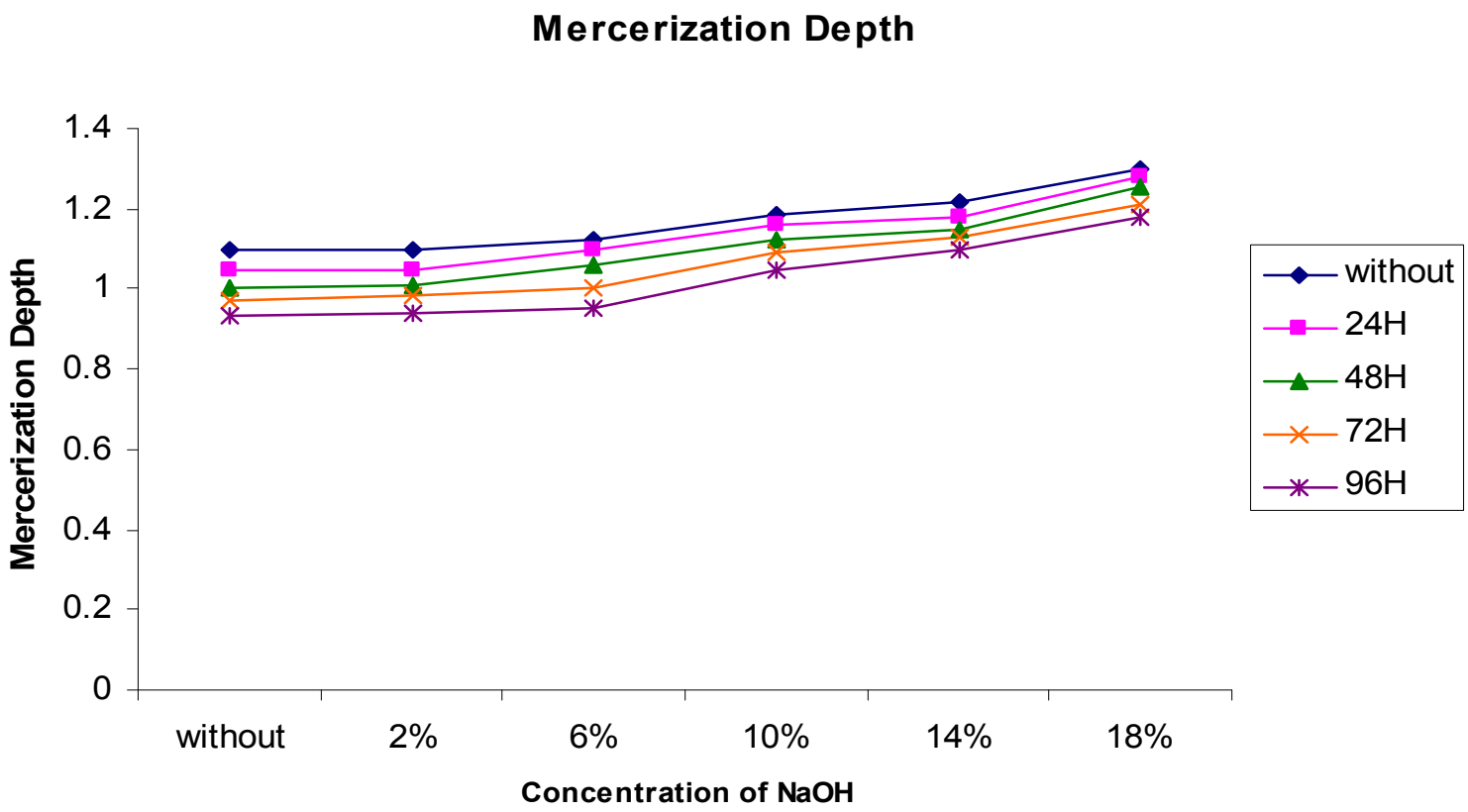


Fig. 21: Effect of both sodium hydroxide concentration and aging time on the mercerization depth by FTIR

5.3. Relative absorbance:

From the data cited in table 16 and fig. 22, it can be seen that a slight degradation of ether linkage [(1-4) β-O-Y linkage] occurred by heating of cellulose at 100 ^{o}C for different times. This is attributed to the degradation occurred in the amorphous region which causes degradation in β-O-Y linkage.

On the other hand, the relative absorbance of β-O-Y linkage at 1112 cm^{-1} increased by increasing concentration of sodium hydroxide solutions. This is attributed to the fact that sodium hydroxide dissolved the small chains of carbohydrate of cellulose molecules, which in turn, causes an increase of the ratio of the chains of high length. This is confirmed by the increase in the degree of polymerization of the treated cellulose with sodium hydroxide.

Table 16: Effect of both sodium hydroxide concentration and aging time on the relative absorbance by FTIR

Conc. of NaOH / Thermal Time	**Without**	**2%**	**6%**	**10%**	**14%**	**18%**
without	1.650	1.743	1.816	1.917	1.951	2.046
24 hrs	1.600	1.656	1.700	1.805	1.886	1.960
48 hrs	1.480	1.605	1.637	1.710	1.783	1.861
72 hrs	1.413	1.508	1.586	1.648	1.732	1.830
96 hrs	1.317	1.413	1.480	1.592	1.670	1.783

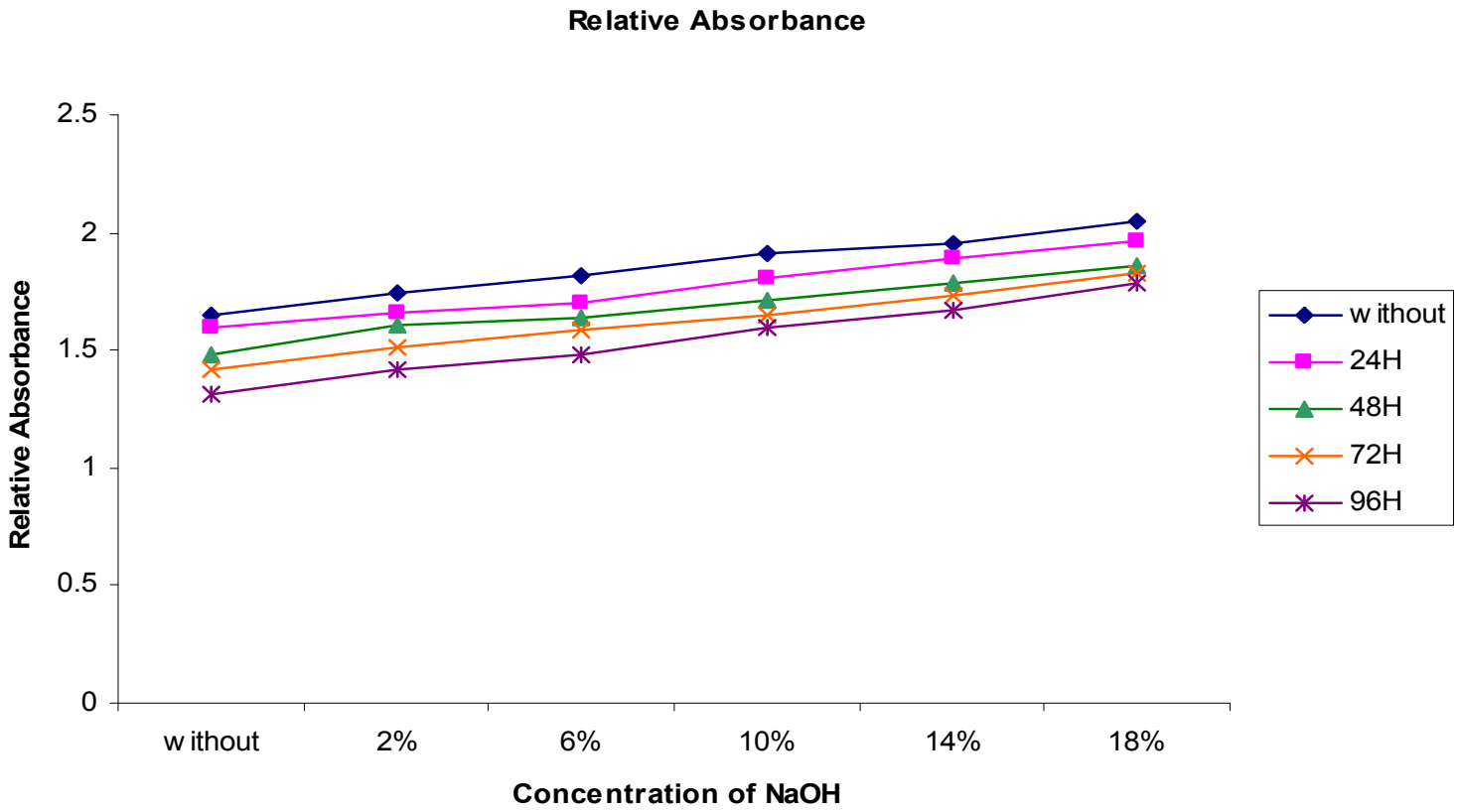


Fig. 22: Effect of both sodium hydroxide concentration and aging time on the relative absorbance by FTIR

6. Super molecular structure of cellulose samples:

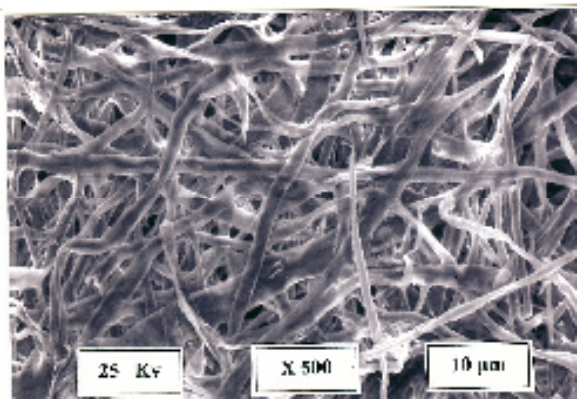
The super molecular structure for the blank, treated with sodium hydroxide and aged samples were studied by electron microscopy. In case of the thermally treated samples for 24 up to 96 hours (fig.22) the fibrils bundles become similar and there is a gradual degree in voids between cellulosic fibers. This indicates that they had good interfacial hydrogen bonding between fibers as a result of dehydration, taking place during the heat treatment (aging) and crystallinity increased during this process (c.f. table 12 and fig.11).

When the samples were treated with different concentration of alkali, the fibers tended to agglomerate gradually into small and large bundles (c.f. fig. 23). Increasing the alkali concentration, the degradation products were more pronounced with large spaces between them as in case of alkali treated pulp with 18 % (fig. 23c). The appearance dates are most likely tiny degraded products which have been carried off during the fracture surface of the paper pulp.

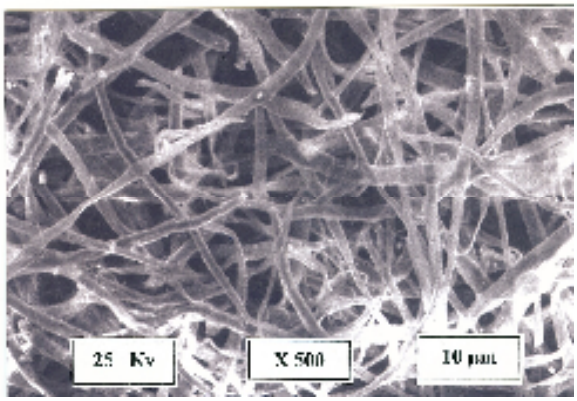
Figs. 24b and 25b illustrated alkali treated samples with 2 % and 18 % alkali concentration respectively and both subjected to thermal treatment for 24 hours. It is clear from these figures that many bundles aggregation showed the decrease of voids between them which confirmed the increase in the degree of polymerization and crystallinity. The increase in the time of thermal treatment for 96 hours either for alkali treated fibers with 2 or 18 % causes increased spaces between the fibers and the samples exhibit large paths with irregularly distributed voids. Figs. 24c, 25c, represent the formation of new accessible non-

cellulosic amorphous fractions which indicate the decrease of crystallinity with increasing the alkali concentration.

a)



b)



c)

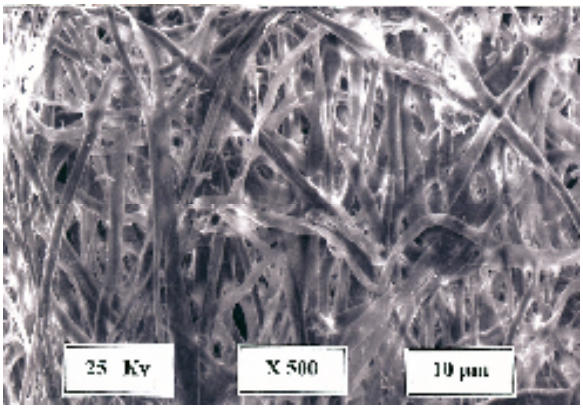
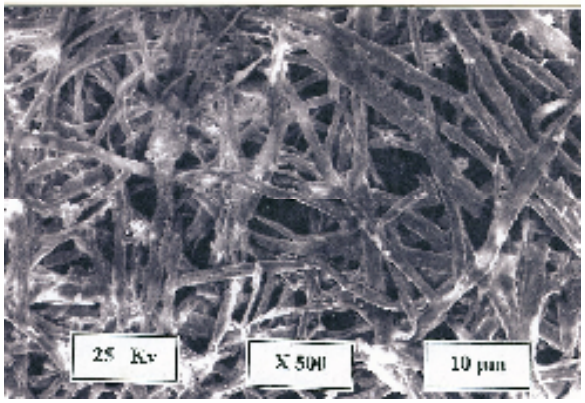
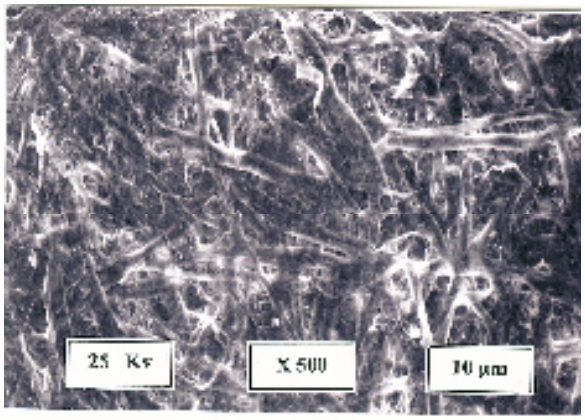


Fig. 22: Scanning electron microscope of fracture surface of kraft wood pulp, a) untreated, b) thermal treated for 24 hrs and c) thermal treated for 96 hrs

a)



b)



c)

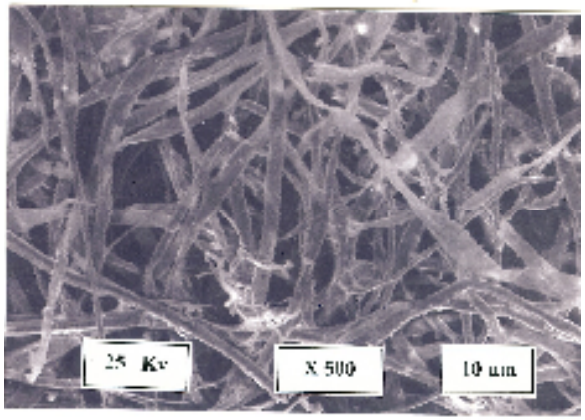
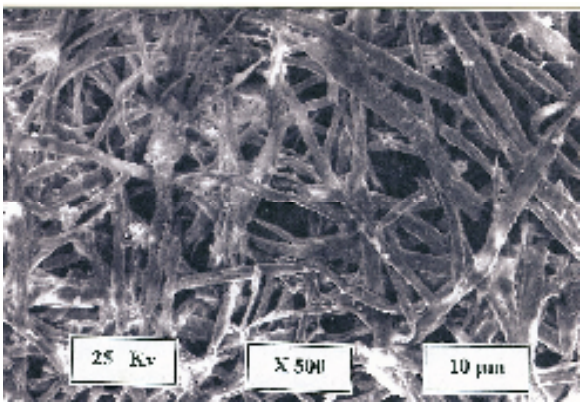


Fig. 23: Scanning electron microscope of fracture surface of alkali treated pulp, a) 2 % NaOH and 0.5 % $ZnCl_2$, b) 10 % NaOH and 0.5 % $ZnCl_2$ and c) 18 % NaOH and 0.5 % $ZnCl_2$

a)



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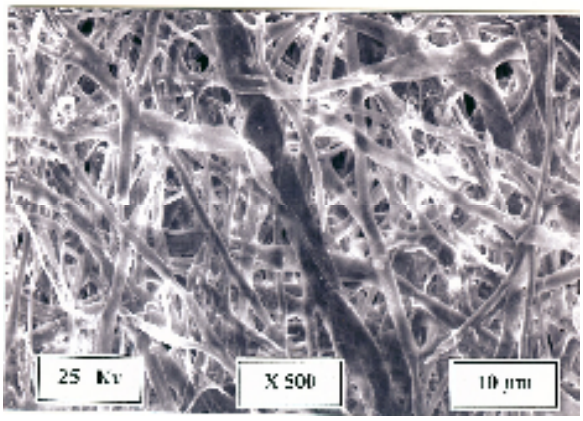


c)

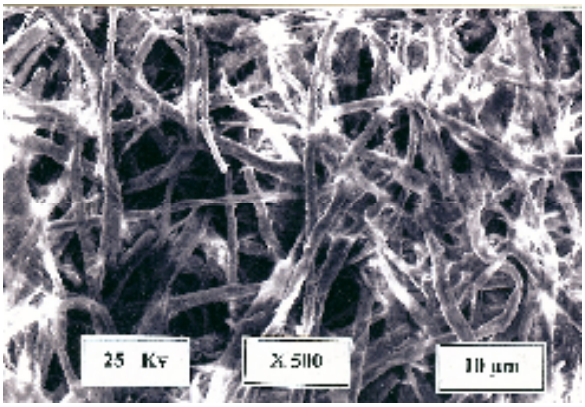


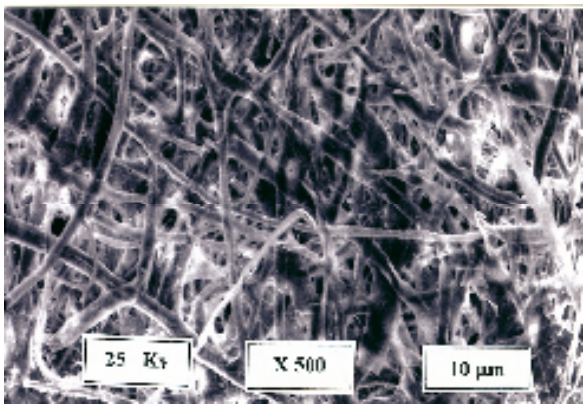
Fig 24: Scanning electron microscope of fracture surface of alkali treated pulp,

a) 2 % NaOH and 0.5 % $ZnCl_2$,

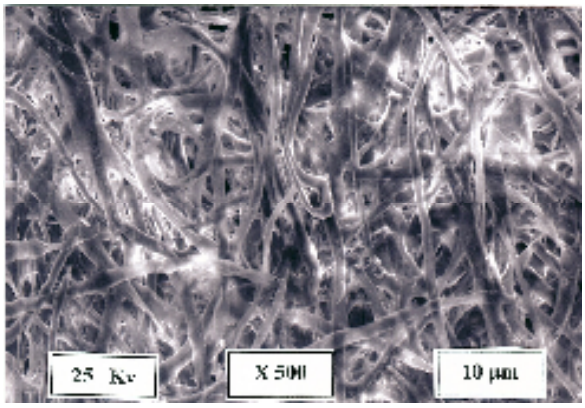
b) alkali treated pulp exposed to thermal treatment for 24hrs and

c) alkali treated pulp exposed to thermal treatment for 96hrs

a)



b)



c)

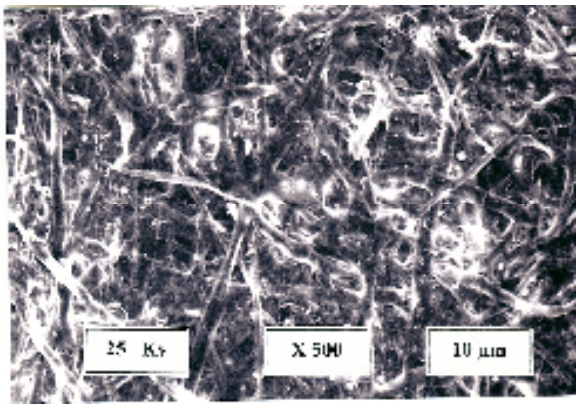


Fig 25: Scanning electron microscope of fracture surface of alkali treated pulp,

a) 18 % NaOH and 0.5 % $ZnCl_2$,

b) alkali treated pulp exposed to thermal treatment for 24 hrs and

c) alkali treated pulp exposed to thermal treatment for 96 hrs

7. Effect of Aging on chemical and optical properties:

7.1. Chemical and optical properties of aged samples without sodium hydroxide treatment:

Table 17: Chemical and optical properties of aged samples without sodium hydroxide treatment

Sample no.	Time of heat treatment	-COOH meq./100g	Whiteness %	Opacity %
1	without	96.6	66.7	73.6
2	24 hrs	112.2	66.3	74.5
3	48 hrs	116.3	66.1	74.0
4	72 hrs	122.4	65.6	73.8
5	96 hrs	130.6	63.8	73.2

Table 17 shows the chemical and optical properties of the aged samples without sodium hydroxide treatment. The carboxyl content is 96.6 meq/100 g for the unaged sample; the carboxyl content increased gradually with the increase of the aging time until reaches 130.6 meq/100 g after aging for 96 hours. This increase is normal because the carboxyl content is one of the groups increased with the oxidation process that takes place as the time of aging increased. The carboxyl groups with the other groups produced as a result of oxidation (carbonyl) cause the yellowing of paper samples. This explains the decrease of the sample whiteness occurred which increased as the aging time increased. The unaged sample has a whiteness of 66.7 % and this value decreased as the aging time increased until it reached 63.8 % after 96 hours of aging. The decrease of whiteness (yellowing) by increasing time of aging takes place as a result of the oxidized groups, carboxyl and carbonyl which increased by time of aging.

The opacity percent of the original sample (unheated) is 73.6 %; after heating for 24 hours. The opacity is slightly increased to 74.5 % then decreased after that by increasing aging time till it became 73.2 % after 96 hours aging time. The slight increase that takes place at the first 24 hours of aging may be due to the ordering of cellulose molecule at this time which is accompanied with an increase in the sample crystallinity.

7.2. Chemical and optical properties of pulp samples treated with sodium hydroxide:

Table 18: Chemical and optical properties of pulp samples treated with sodium hydroxide

Sample no.	NaOH Conc.	Yield %	Pentosan %	Lignin %	COOH meq./100g.	Whiteness %	Opacity %
1	without	-	9.5	0.6	96.6	66.7	73.6
6	2 %	96.3	8.5	0.5	93.4	82.2	71.5
11	6 %	94.5	5.2	0.3	91.4	83.6	71.0
16	10 %	91.8	3.4	0.1	87.7	84.0	70.3
21	14 %	87.9	1.2	traces	84.2	84.5	69.3
26	18 %	86.2	0.0	0.0	80.8	83.3	68.2

Table 18 shows the optical and chemical properties of pulp samples treated with sodium hydroxide at different concentrations in presence of 0.5 % $ZnCl_2$. The yield decreased with the increase of sodium hydroxide concentration, this can be attributed to the dissolution of small amounts of polymerized molecules as the sodium hydroxide concentration increased. Also lignin and pentosan dissolved more as the concentration of sodium hydroxide increased. The yield is 96.3 in case of 2 % sodium hydroxide concentration, this value decreased to 86.2 at 18 % sodium hydroxide concentration. This decrease can be attributed to the fact that all pentosan, lignin, beta and gamma-cellulose dissolved in 18 % sodium hydroxide solution. Since the α-cellulose determination takes place at 17.5 % sodium hydroxide concentration, as stated above, the lignin goes from 0.6 % to practically zero as the sodium hydroxide increased to 18 %, also the pentosan (hemicellulose) talls from 9.5 to zero as the sodium hydroxide increased to 18 %.

The carboxyl content of the original sample was 96.6 meq/100 g pulp; decreased to about 80.8 meq/100 g for the sample treated with 18 % sodium hydroxide. This decrease is due to the fact that when the cellulose is treated with sodium hydroxide all the carboxyl contents are neutralized to the sodium salt which can not be transferred back to carboxyl groups when sample is washed after the treatment.

The whiteness of the original sample is 66.7 % and increased markedly to 82.2 % when the sample was treated with 2 % sodium hydroxide. This increase is due to the strong effect of sodium hydroxide as a refiner even at low concentration. The increase is still effective up to 14 % sodium hydroxide concentration when the whiteness reaches 84.5 %. Increasing sodium hydroxide up to 18 % gives a slight decrease in the whiteness to 83.3%, this is due to the strong effect of sodium hydroxide at this concentration as a mercerizing agent.

The opacity of the untreated sample was 73.6 % which decreased to 71.5 % after treatment with 2 % sodium hydroxide solution due the refining effect of the sodium hydroxide. By increasing the sodium hydroxide concentration the value of the opacity decreased as a result of refining and mercerizing effects of the sodium hydroxide solution; at 18 % sodium hydroxide the opacity is only 68.2 %.

7.3. Chemical and optical properties of samples treated with 2 % sodium hydroxide and aged for different times:

Table 19: Chemical and optical properties of samples treated with 2 % sodium hydroxide and aged for different times

Sample no.	Time of heat treatment	-COOH meq./100g	Whiteness %	Opacity %
6	without	93.4	82.2	71.5
7	24 hrs	96.3	73.6	70.2
8	48 hrs	103.4	73.2	69.8
9	72 hrs	108.8	71.4	69.6
10	96 hrs	122.3	70.8	69.1

Table 19 shows the chemical and optical properties of samples treated with 2 % sodium hydroxide and aged for different times. For the carboxyl content, it was 93.4 meq/100 g for the sample treated with 2 % sodium hydroxide without aging. Aging for 24 hours raised the value of carboxyl content to 96.3 meq/100 g; increasing the aging time for 96 hours increase the carboxyl content to 122.3 meq/100 g. Thus we can say that aging of samples treated with 2 % sodium hydroxide for 96 hours increased the carboxyl content by about 34 % as a result of oxidation takes place during the aging of these samples.

For optical properties; whiteness which is 82.2 % for the sample treated with 2 % sodium hydroxide without aging decreased to 73.6 % after 24 hours aging and continue to decrease to 70.8 % only after 96 hours aging. The decrease in percentage is about 17 % as a result of aging for 96 hours for samples treated with 2 % sodium hydroxide. The

opacity also decreased from 71.5 % for the unaged sample to 69.1 % for the samples aged for 96 hours. This is to say that a decrease of the opacity of about 3.4 % resulted after aging samples through treatment with 2 % sodium hydroxide for 96 hours.

7.4. Chemical and optical properties of samples treated with 6% sodium hydroxide and aged for different times:

Table 20: chemical and optical properties of samples treated with 6 % sodium hydroxide and aged for different times

Sample no.	Time of heat treatment	-COOH meq./100g	Whiteness %	Opacity %
11	Without	91.4	83.6	71.0
12	24 hrs	96.4	74.8	68.0
13	48 hrs	101.4	73.7	67.6
14	72 hrs	109.5	72.6	67.0
15	96 hrs	119.7	72.0	66.7

Table 20 illustrates the chemical and optical properties of samples treated with 6 % sodium hydroxide and aged for different times up to 96 hours. Sample treated with 6 % sodium hydroxide only has a carboxyl content of 87.7 meq/100 g. Aging the sample for 24 hours raised the carboxyl content to 91.4 meq/100 g, this value still increased until it reach 119.7 meq/100 g after aging for 96 hours. The carboxyl content increased by about 36 % as the aging time was increased to 96 hours.

The whiteness of the samples treated with 6 % sodium hydroxide is 83.6 %, after 24 hours aging the whiteness decreased to 74.8 %. By increasing the aging time, the whiteness decreased till it reached 72 % after 96 hours aging time. From the above values, it is clear that increasing the aging time to 96 hours, the whiteness decreased by about 17 %.

For the opacity of samples treated with 6 % sodium hydroxide, it amounted to 71 %; this value decreased as the aging time increased until it reached 66.7 % after 96 hours aging. Thus the opacity decreased by about 5 % as a result of increasing the aging time to 96 hours.

7.5. Chemical and optical properties of samples treated with 10 % sodium hydroxide and aged for different times:

Table 21: Chemical and optical properties of samples treated with 10 % sodium hydroxide and aged for different times

Sample no.	Time of heat treatment	-COOH meq./100g	Whiteness %	Opacity %
16	Without	87.7	84.0	70.3
17	24 hrs	89.7	87.3	67.1
18	48 hrs	96.3	77.6	66.4
19	72 hrs	100.2	77.0	65.8
20	96 hrs	109.0	76.3	65.2

Table 21 illustrates the chemical and optical properties of samples treated with 10 % sodium hydroxide and aged for different times up to 96 hours. For the carboxyl content, it was 87.7 meq/100 g for the sample treated with 10 % sodium hydroxide without aging. After aging for 24 hours, it increased to 89.7 meq/100 g and still increased as the time of aging was increased till it reached 109 meq/100 g after 96 hours of aging. From the above values, we can conclude that the carboxyl content increased by about 24 % as a result of aging to 96 hours.

Whiteness decreased as the aging time was increased; sample without aging gave 84 % whiteness and decreased with increasing aging time until it reached 76.3 % after aging for 96 hours. The decrease of whiteness due to increasing aging time to 96 hours is about 10 %. The decrease of whiteness is due to the increase of oxidized groups in pulp

specially carboxyl and carbonyl groups which cause yellowing of the samples and hence the whiteness decreased.

The opacity also decreased as the aging time was increased, the unaged sample has a value of 70.3 % opacity and the aged sample for 96 hours gives only 65.2 % with a decrease of about 10 %.

7.6. Chemical and optical properties of samples treated with 14% sodium hydroxide and aged for different times:

Table 22: Chemical and optical properties of samples treated with 14 % sodium hydroxide and aged for different times

Sample no.	Time of heat treatment	-COOH meq./100g	Whiteness %	Opacity %
21	Without	84.2	84.5	69.3
22	24 hrs	86.2	79.2	66.1
23	48 hrs	90.4	78.7	64.7
24	72 hrs	94.2	77.4	63.9
25	96 hrs	102.2	77.1	63.3

Table 22 shows the effect of aging on the chemical and optical properties of samples treated with 14 % sodium hydroxide. Sample without aging has 84.2 meq/100 g carboxyl content, this value increased with increasing aging time till it reached 102.2 meq/100 g after 96 hours aging. Aging for 96 hours increased the carboxyl content by about 18 %, this can be attributed to the oxidation of cellulosic groups to produce carboxyl and carbonyl groups which increased by increasing the aging time.

For whiteness of the aged sample, amounts to 84.5 % for thermally untreated sample and this value decreased as the aging time was increased till reaches 77.1 % after 96 hours aging. The decrease in whiteness amounted to 10 % of its original value as a result of aging for 96 hours. Decrease in whiteness can be attributed to the oxidation of the group which increased by increasing aging time and it is well known that this groups cause yellowing of the cellulose samples.

Opacity of unaged sample amounted to 96.3 % and this value decreased as the aging time was increased till it reached 63.3 % after 96 hours aging. The decrease in opacity as a result of aging for 96 hours amounts to 9.5%.

7.7. Chemical and optical properties of samples treated with 18% sodium hydroxide and aged for different times:

Table 23: Chemical and optical properties of samples treated with 18 % sodium hydroxide and aged for different times

Sample no.	Time of heat treatment	-COOH meq./100g	Whiteness %	Opacity %
26	Without	80.8	83.3	68.2
27	24 hrs	81.9	70.4	67.8
28	48 hrs	84.3	69.6	64.1
29	72 hrs	90.6	67.8	62.6
30	96 hrs	99.3	66.9	61.4

Table 23 illustrates the chemical and optical properties of samples treated with 18 % sodium hydroxide and aged for different times up to 96 hours. Sample treated with 18 % sodium hydroxide only has a carboxyl content of 80.8 meq/100 g. Aging of the sample for 24 hours raised the carboxyl content to 81.8 meq/100 g, this value still increased until reaches 99.3 meq/100g after aging for 96 hours. The carboxyl content increased by about 23 % as the aging time was increased to 96 hours.

Whiteness decreased as the aging time was increased; sample without aging gives 83.3 % whiteness and decreased with increasing aging time until it reached 66.9 % after aging for 96 hours. The decrease of whiteness due to increasing aging time to 96 hours is about 24.5 %. The decrease in whiteness is due to the increase of oxidized groups in pulp specially carboxyl and carbonyl groups which cause yellowing of the samples and hence the whiteness decreased.

The opacity also decreased as the aging time was increased, the unaged sample has 68.2 % opacity and the aged sample for 96 hours gave only 61.4 % with a decrease of about 11 %.